Homochiral Ion-Pairing Assisted by $\pi-\pi$ Stacking between Δ-[Ru(bpy)$_2$(Hcmbpy)]$^{2+}$ and Δ-Trisphat: A Quantitative Investigation

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The ion-pairing between the chiral Δ- or Λ-[Ru(bpy)$_2$(Hcmbpy)]$^{2+}$ (Δ**1** or Λ**1**) and the Δ-Trisphat$^-$ (Δ**2**) (Hcmbpy = 4-carboxy-4′-methyl-2,2-bipyridine and Trisphat = tris(tetrachlorobenzenediolato)phosphate(V)) is investigated in solution by means of ^{1}H NMR spectroscopy. The Ru−Trisphat ion-pairing adopts two stoichiometries that exchange via a fast dynamic process. The equilibrium constants K and K' are calculated for the 1/1 and 1/2 Ru/Trisphat stoichiometries. The constant values are in agreement with Coulombic attractions assisted by a $\pi-\pi$ stacking between the bpy ligands of the Ru cation and the aromatic rings of the Trisphat anion. The homochiral pairing is favored as opposed to the heterochiral one, as shown by the respective K' values of 4.46×10^5 vs 2.05×10^5 M^{-2}. In the homochiral ion pair, the cationic and anionic propellers adequately fit to optimize the π-stacking interactions and to lead to a dication sandwiched by two anions at the highest Trisphat/Ru ratios.

In the last decades, chiral resolution of enantiomers from a racemic mixture has been one of the major challenges for chemists. In the field of coordination chemistry, chiral cations of octahedral metal complexes have been designed for diverse functions in biological and chemical systems, including the intercalation of metal complexes into DNA.[1] Further, the metal complexes of C_2-symmetry were involved in asymmetric catalysis,[2] etc. In solution, an efficient strategy to separate such chiral cations associated with traditional achiral anions (PF_6^-, BF_4^-, etc.) consists in exchanging the common anions for chiral versions. The induction of optical activity by chiral anions onto cationic racemic organometallic substrates has recently regained a new interest.[3] The association of racemic cations with enantiopure counterions leads to the formation of diastereomeric ion pairs, which present different chemical and physical properties.

The field of coordination chemistry reports many examples where the tight association of charged species proceeds typically from either $\pi-\pi$ stacking interactions or hydrogen bonding. An interesting example of association via $\pi-\pi$ stacking is given through the octahedral eilatin complexes [M(L−L)$_2$(eilatin)]$^{2+}$ (M = Ru, Os; L−L = bpy, phen), where eilatin is a heptacyclic aromatic ligand with a strong π-character.[4] The crystallographic structure shows that a heterochiral association is formed between Δ-[M(L−L)$_2$(eilatin)]$^{2+}$ and Λ-[M(L−L)$_2$(eilatin)]$^{2+}$ cations (Figure 1A).[5] In a previous work, we reported the X-ray structure of the dicarboxylic complex [Ru(bpy)$_2$(H2dcbpy)]$^{2+}$, where a double-chained 1D-polymer encloses strong H-bonds. The supramolecule is built from blocks linked to one another via H-bonds; a block itself results from a Δ-[Ru(bpy)$_2$(H2dcbpy)]$^{2+}$ cationic unit connected to a Λ-[Ru(bpy)$_2$(H2dcbpy)]$^{2+}$ cationic unit by two H-bonds of equal distances with $d(\mathrm{O}\cdots\mathrm{O}) = 2.60$ Å (Figure 1B).[6] These two examples provide evidence that despite the electrostatic repulsions between the cationic actors, H-bonding and $\pi-\pi$ stacking interactions allow such associations to be tightened.

On the other hand, if the charged species are one cation and one anion, the Coulombic attractions may be reinforced by the above-mentioned interactions if the associates are targeted to this end.

Here, we have chosen to study the association between the chiral Δ- or Λ-[Ru(bpy)$_2$(Hcmbpy)]$^{2+}$ (Δ**1** or Λ**1**) and the Δ-Trisphat$^-$ (Δ**2**) (Hcmbpy = 4-carboxy-4′-methyl-2,2-bipyridine and Trisphat = tris(tetrachlorobenzenediolato)phosphate(V)) (Scheme 1). No crystal structure has been reported so far; thus quantitative information relative to the association is poor. In this work, the stoichiometry of the ion-pairing is examined by NMR spectroscopy. The association constants are calculated for each diastereomeric ion pair. The geometry of the pairing is discussed according to the chirality and the symmetry of the partners.

Results and Discussion

The Trisphat anion **2** (Λ or Δ enantiomer) has been confirmed to be a valuable chiral NMR shift reagent for differentiation and resolving enantiomers as well as for asymmetric induction

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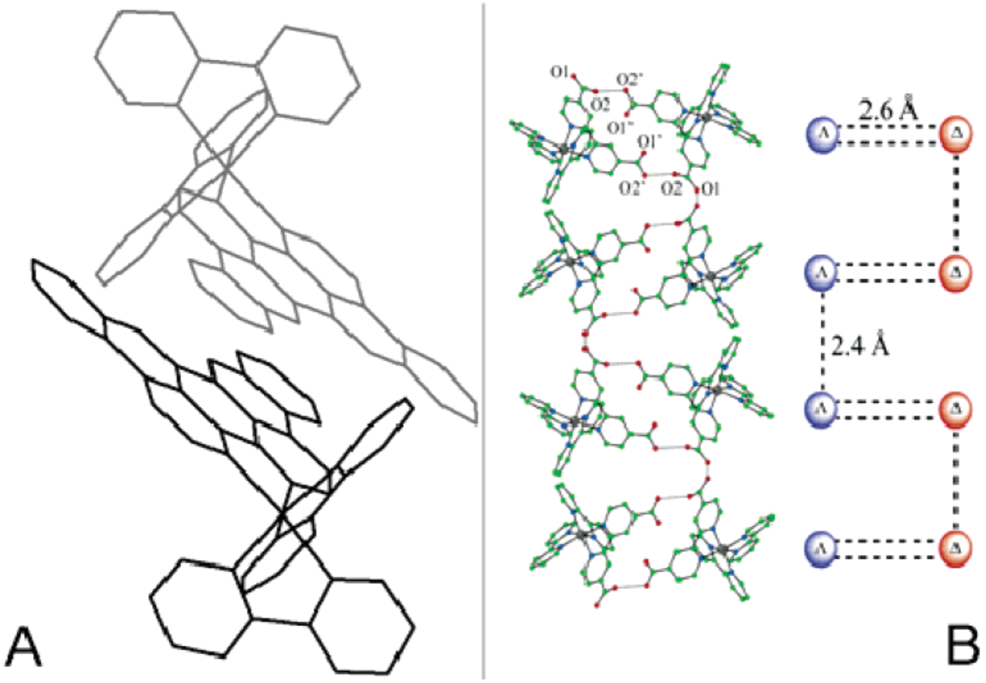
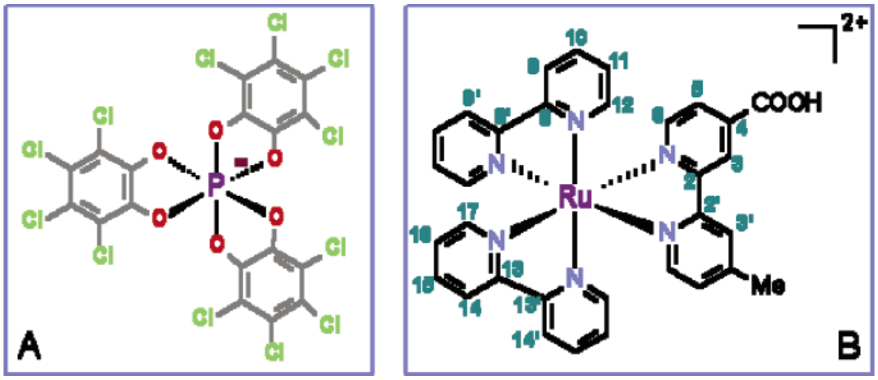


Figure 1. Association of cationic metallic complexes by either π−π stacking interactions (A) or H-bonding (B).

Scheme 1. (A) Δ-Trisphat (Δ-tris(tetrachlorobenzenediolato)phosphate(V)) and (B) Λ-[Ru(bpy)$_2$(Hcmbpy)]$^{2+}$ Including the Atom Numbering[a]



[a] Only the anion and cation are given (A and B, respectively)

reactions.[7] In a previous work, we reported the synthesis, the characterization, and the chiral resolution of the ruthenium cationic complexes [Ru(bpy)$_2$(Hcmbpy)]$^{2+}$ (Λ**1** and Δ**1**), where one of the bipyridyl ligands carries one carboxylic acid functionality (Hcmbpy).[8] We showed briefly and qualitatively that a homochiral association occurs between the Δ-Trisphat and Δ-[Ru(bpy)$_2$(Hcmbpy)]$^{2+}$. In this work, we have undertaken a complete investigation of these species in solution by ^{1}H NMR techniques and are able to get precise and quantitative information on the homo- and heterochiral ion-pairings. For instance, the association constants are determined for both homo- and heterochiral assemblies.

We have decided to work on the diastereomerically pure salts Λ**1**−Δ**2** and Δ**1**−Δ**2** using ^{1}H NMR spectroscopy. As the Δ-Trisphat anion is a "silent" probe for the proton investigation, no interspecies signal overlap is possible and the set of observable signals is readily assigned to the Ru compounds.

Dimerization. Many examples of self-association in solution and in solid state of cationic octahedral metal complexes with extended aromatic ligands have been reported.[4,9] Since the goal of our work is to study the Ru−Trisphat ion-pairing, it was necessary to check that no other equilibria (self-association) concurrent with the ion-pair association exist under our experimental conditions, thus avoiding additional species such as dimers in the solution.

For our purpose investigations, we kept the concentrations as low as possible for enantiomeric [Ru] = [**1**]$_0$ and [Δ-Trisphat] = [**2**]$_0$ {where [**1**]$_0$ is the known total concentration of Ru and [**2**]$_0$ is the known total concentration of Δ-Trisphat}.

On the contrary, we performed a "forced self-association" experiment where low and much higher concentration solutions

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Table 1. Diffusion Coefficients for Δ1 in 90/10 CD_2Cl_2/CD_3CN at Two Monomeric Molar Concentrations (283 K)[a]

signal	$D \pm \Delta D$ coefficient × 10^9 m^2 s^{-1} 0.3 mM	$D \pm \Delta D$ coefficient × 10^9 m^2 s^{-1} 9.0 mM
$CHDCl_2$ (solvent)	6.15 ± 0.01	6.23 ± 0.01
H3	4.24 ± 0.46	4.61 ± 0.03
CH_3	4.32 ± 0.03	4.37 ± 0.01

[a] H3 and CH_3 are selected as probes for the Hcmbpy ligand of the chiral Ru complex.

were prepared for both Ru complexes and Trisphat. For the enantiopure Ru complexes, ^1H NMR spectra recorded at $[\mathbf{1}]_0 = 0.3$ and 10.0 mM in a CD_2Cl_2/CD_3CN solvent mixture (90/10) show no significant chemical shift variation at 283 K. For Δ-Trisphat, three samples at $[\mathbf{2}]_0 = 0.5$, 5.0, and 50.0 mM (same solvents) display identical ^1H NMR spectra within the error margin due to the spectral resolution (see Experimental Section).

As the state of self-association of a molecule and/or ionic aggregation[10] in solution can also be ascertained from the diffusion coefficients, a series of pulsed field gradient NMR (PFGNMR) diffusion measurements have been executed for the Δ**1** enantiomer, as an example, in the concentration range chosen for the "forced self-association" study (exactly $[\Delta\mathbf{1}]_0 = 0.3$ and 9.0 mM). Diffusion constants, *D*, from the ^1H NMR spectra in the CD_2Cl_2/CD_3CN solvent mixture (90/10) at 283 K are given in Table 1. Typical plots of the signal intensity vs the square of the gradient strength together with the calculated curves (see Experimental Section for details) are displayed as Supporting Information. The results show that the concentration dependence of the *D* values is extremely minor within the explored range. This indicates that the average level of aggregation of the chiral Ru cations remains unchanged from 0.3 to 9 mM. At 0.3 mM, a state where all the cations would be self-associated is unlikely.

Consequently, the assumption of a self-association (dimerization) is precluded in the experimental conditions of the main study for both species. A chemical shift change is then reliable for the heterospecies binding.

Stoichiometry Determination of the Chiral Ion-Pairing. Prior to any determination of association constant it is essential to ascertain the stoichiometry of the Ru−Trisphat complex. This has been achieved from NMR data by means of the method of continuous variations, known as Job's method.[11] This method involves preparing a series of solutions containing the enantiopure Ru (Λ**1** or Δ**1**) and Δ-Trisphat in varying proportions so that the complete range of mole ratios is covered ($0 < [\mathbf{1}]_0/([\mathbf{1}]_0 + [\mathbf{2}]_0) < 1$ by 0.1 step). The total concentration $[\mathbf{1}]_0 + [\mathbf{2}]_0$ remains constant at 2.5 mM for each sample in the CD_2Cl_2/CD_3CN (90/10) solvent mixture.

For each series (Λ**1** + Δ**2** and Δ**1** + Δ**2**), NMR spectra at 283 K reveal a set of signals that experience a frequency shift as a function of the $[\mathbf{1}]_0/([\mathbf{1}]_0 + [\mathbf{2}]_0)$ ratio. This behavior, previously depicted,[8] is attributed to a fast exchange process between the free Ru enantiomer (Λ**1** or Δ**1**) and the Ru enantiomer associated with the Trisphat to lead to the Δ**1**−Δ**2** or Λ**1**−Δ**2** diastereomer. As expected and previously described, the spectrum corresponding to each diastereomeric pair deviates from the other, at the same ratio.

After the peak frequency is determined, a Job plot is built for three selected signals from each pair (Me, H5′, H9 for Δ**1** + Δ**2** and Me, H3′, H6′ for Λ**1** + Δ**2**) as shown in Figure 2.

Surprisingly, the curves reach a maximum for a ratio value on the upper side of 0.4. For the 1/1 and 1/2 Ru/Trisphat stoichiometries, the maximum is centered at 0.5 and 0.33, respectively. The observed value corresponds to the average value of these two stoichiometries (0.5 + 0.33)/2 = 0.415. In solution, the 1/1 and 1/2 stoichiometries exist. Due to the fast exchange dynamic, a pairing where one Ru species is associated with one Trisphat (**1**−**2**) is in equilibrium with a pairing of one Ru species with two Trisphat (**2**−**1**−**2**). It seems that for such octahedral metal complexes incorporating bpy aromatic ligands for which the electrons are fully delocalized, the global charge of the system is not strictly reliable for a stoichiometry determination. The π-electrons of the bpy ligands are partly transferred to the cationic metal center via efficient orbital overlaps.

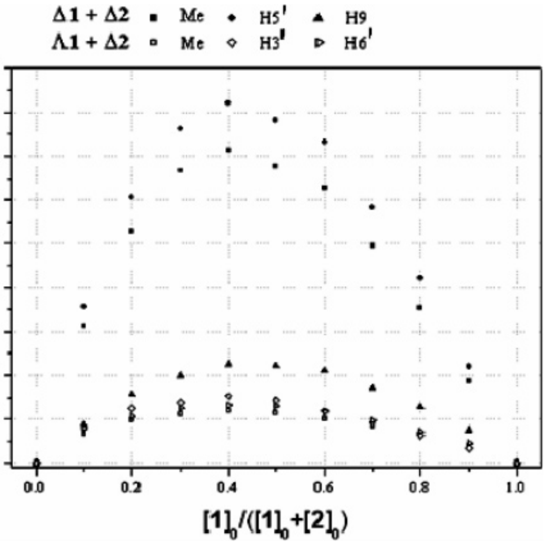

Figure 2. Job plots for the Δ**1** + Δ**2** and Λ**1** + Δ**2** mixtures. Curves giving the variation of chemical shift (Δδ in Hz) × $[\mathbf{1}]_0$ (M) vs the $[\mathbf{1}]_0/([\mathbf{1}]_0 + [\mathbf{2}]_0)$ mole ratio are displayed for selected signals from the ^1H NMR spectra at 283 K. Solid symbols refer to the Δ**1** + Δ**2** mixture, empty symbols to Λ**1** + Δ**2**. The criteria for the signals selection are (i) well-resolved signals over the full 0−1 ratio domain and (ii) signals that experience significant frequency change to accurately probe the pairing.

Since Δ**1** signals (vs Λ**1**) are the most sensitive to the Δ**2** addition, we expect that the Δ**1**−Δ**2** pairing is stronger.

Association Constants. Six milliliters of stock solutions of Λ**1** and Δ**1** were prepared (0.3 mM in CD_2Cl_2/CD_3CN, 90/10). Aliquots (500 μL) of each stock solution were added to an NMR tube initially containing an amount of solid Δ-Trisphat in order to obtain a wide Δ-Trisphat concentration range ($[\mathbf{2}]_0 = 0$, 0.2, 0.4, 0.7, 1.0, 2.0, 5.0, 7.0, 10.0, 20.0, and 50.0 mM) for a constant Ru concentration $[\mathbf{1}]_0$ (see Experimental Section for details). The ^1H NMR spectra at 283 K are given in Figure 3.

A brief examination of the two series of spectra highlights the different behavior of Λ**1** and Δ**1** upon Δ**2** addition. While the Δ**1** series undergo strong signal frequency shifts (Figure 3B), the Λ**1** series are poorly perturbed (Figure 3A). More important is the discrepancy between the signal splitting of the two series when Δ**2** is present at high, 2/1 ratios. Δ**1** spectra exhibit a number of signals that is adequate with a real C_1-symmetry when associated with Δ**2** (1 mM and above). Substituted as well as unsubstituted bpy ligand signals are spread

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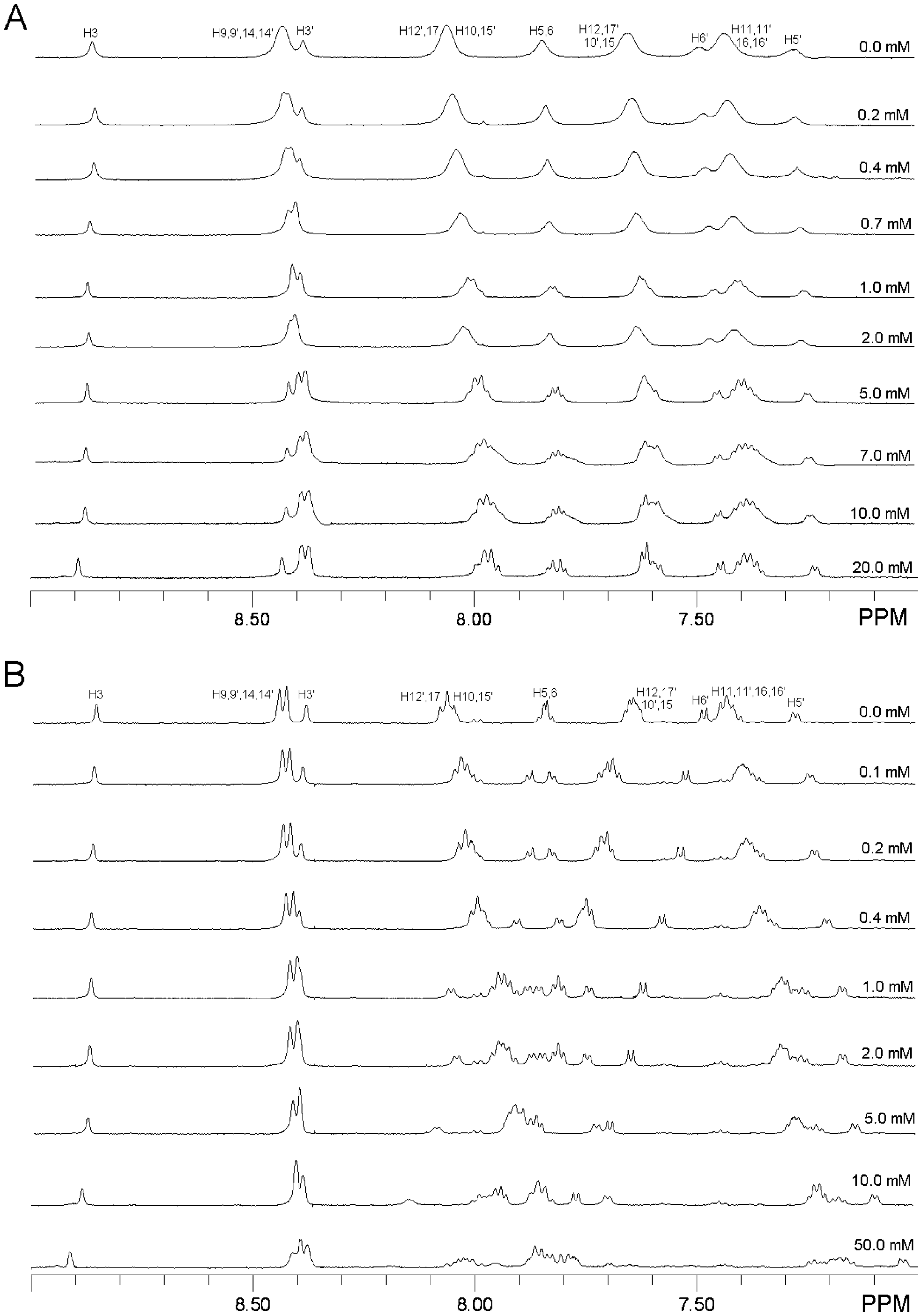

Figure 3. ^{1}H NMR subspectra of 0.3 mM solutions of **1** in CD_2Cl_2/CD_3CN, 90/10, at various Δ-Trisphat concentrations (283 K). (A) Titration of Λ**1** by Δ**2**. (B) Titration of Δ**1** by Δ**2**. Only the aromatic region is displayed.

out; that is, every proton experiences a distinguishable magnetic environment as the amount of Δ**2** increases. Δ**1** and Δ**2** associate as an intimate ion pair. On the contrary, the number of signals in series A is reduced, in agreement with the protons of the unsubstituted bpy ligands being rendered "magnetically similar" by fast rotational motions of the complex in solution. These "undercrowded" spectra even when the Δ**2** concentration is high indicate that the Λ**1**−Δ**2** association is weak.

With the knowledge of the stoichiometries, association constants have been calculated for binary and ternary systems using a curve-fitting approach. For the 1/1 stoichiometry, the association constant is given as

$$\mathbf{1} + \mathbf{2} \rightleftharpoons \mathbf{1{-}2} \qquad K = [\mathbf{1{-}2}]/[\mathbf{1}][\mathbf{2}]$$

Only two parameters, K and $\delta_{\mathbf{1-2}}$ (with $\delta_{\mathbf{1-2}}$ being the chemical shift of the selected proton in the 1/1 Ru/Trisphat pairing), are unknown. Solutions are provided by solving the general equation in Chart 1.

Chart 1

$$[\mathbf{1{-}2}] = \frac{(K[\mathbf{2}]_0 + K[\mathbf{1}]_0 + 1) - \sqrt{\{(K[\mathbf{2}]_0 - K[\mathbf{1}]_0)^2 + 2K[\mathbf{2}]_0 + 2K[\mathbf{1}]_0 + 1\}}}{2K}$$

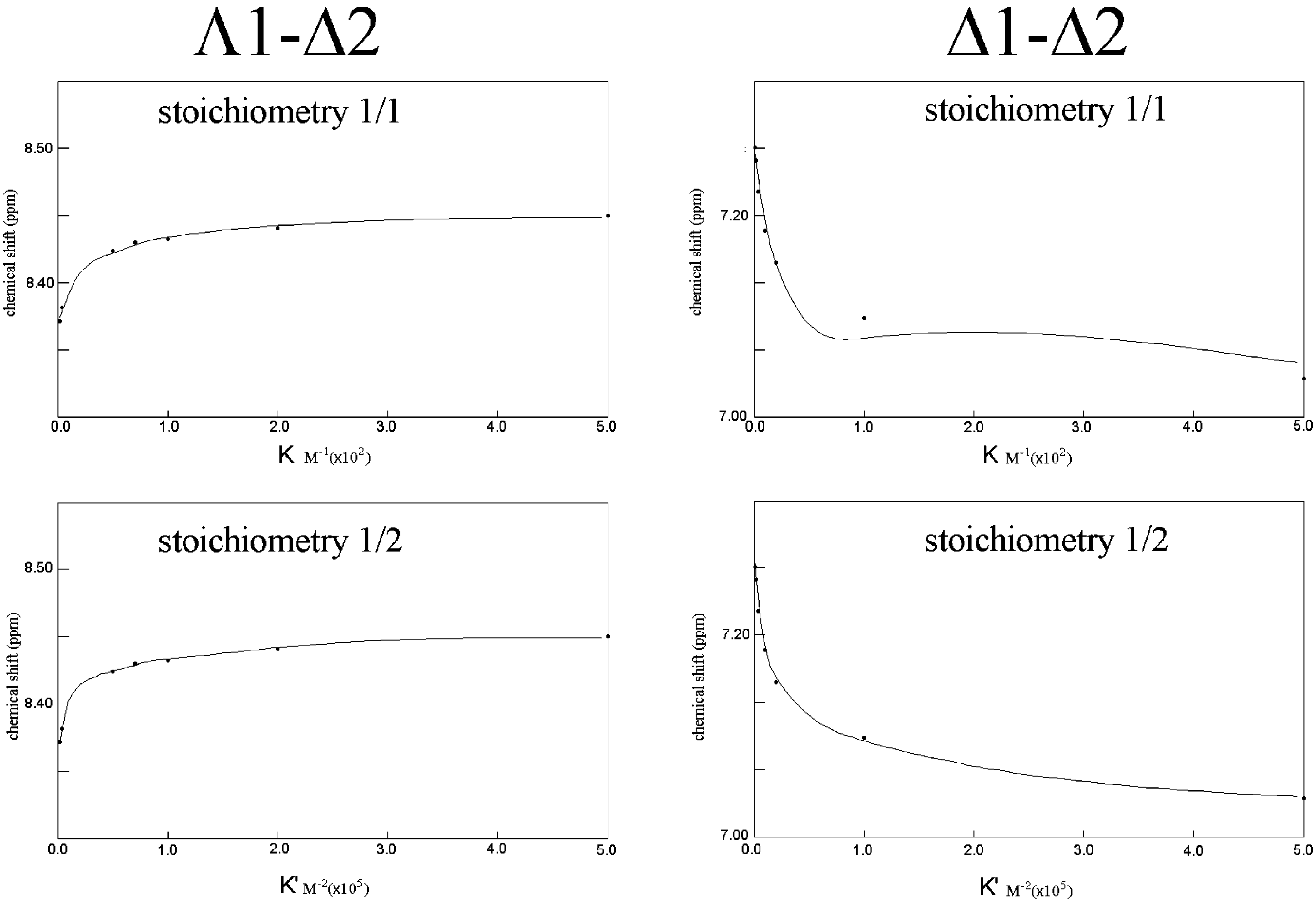

Figure 4. NMR data fits considering either the binary system (1/1 Ru/Trisphat) or the ternary system (1/2 Ru/Trisphat) by means of the WinEqnmr program. Fits for the protons H5′ from **Δ1** and H3′ from **Λ1** are displayed.

Table 2. Example of the Application of Both Binary and Ternary Models to the NMR Data Sets for the Δ1 + Δ2 and Λ1 + Δ2 Mixtures in CD_2Cl_2/CD_3CN (90/10) at 283 K[a]

	1/1 stoichiometry			1/2 stoichiometry					
	K (M^{-1})	δ_{1-2} (ppm)	R-factor (%)	K_1 (M^{-1})	δ_{1-2} (ppm)	K_2 (M^{-1})	δ_{2-1-2} (ppm)	K' (M^{-1})	R-factor (%)
Δ1−**Δ2**	6.17×10^{2} (±30%)	7.041	0.1355	4.84×10^{3} (±2%)	7.147	9.2×10^{1} [b]	7.010	4.46×10^{5} (±2%)	0.0408
Λ1−**Δ2**	3.41×10^{2} (±6%)	8.441	0.0141	1.95×10^{3} (±2%)	8.418	1.05×10^{2} [b]	8.443	2.05 ± 10^{5} (±2%)	0.0073

[a] H5′ and H3′ are selected for the calculation of the association constants of **Δ1** + **Δ2** and **Λ1** + **Δ2**, respectively. [b]As K_2 is not given by WinQENMR, the error is not known.

The 1/2 Ru/Trisphat stoichiometry includes two equilibrium constants:

$$\mathbf{1} + \mathbf{2} \rightleftharpoons \mathbf{1\text{-}2} \qquad K_1 = [\mathbf{1{-}2}]/[\mathbf{1}][\mathbf{2}]$$

$$\mathbf{1{-}2} + \mathbf{2} \rightleftharpoons \mathbf{2{-}1{-}2} \qquad K_2 = [\mathbf{2{-}1{-}2}]/[\mathbf{1{-}2}][\mathbf{2}]$$

The association constant is defined as

$$K' = K_1K_2 = [\mathbf{2{-}1{-}2}]/[\mathbf{1}][\mathbf{2}]^2$$

Four parameters are unidentified (K_1, K_2, $\delta_{\mathbf{1-2}}$, and $\delta_{\mathbf{2-1-2}}$, where $\delta_{\mathbf{2-1-2}}$ is the chemical shift of the selected proton in the 1/2 Ru/Trisphat pairing), and more complicated cubic equations are necessary to solve the system. The curve-fitting approach was applied by means of the WinEQNMR program.[12] This program has been stated to be a valuable tool for elucidating the association constants within ternary systems from NMR data.[13] Moreover, it has been tested for the Ru octahedral cations, namely, $[Ru(Me_2bpy)_3]^{2+}$ paired to classic achiral anions.[14]

For each diastereoisomeric pair, the frequency of selected peaks was determined for the various $[\mathbf{1}]_0/[\mathbf{2}]_0$ ratios. Signals were chosen according to the following criteria: (i) they remain “isolated” from other signals over the titration course; (ii) they experience a significant frequency shift when the **Δ2** amount increases in order to accurately probe the pairing. As an example, one couple of data fitting is displayed for both diastereoisomers in Figure 4, and the parameter output values can be found in the Supporting Information. The pertinence of the fits for each data set was judged according to the *R*-factor (as defined in the Experimental Section). The association constants and the calculated chemical shifts are summarized in Table 2. Applying the 1/1 model to the experimental data does not lead to a conclusive fit according to the error margin on *K*

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vs K_1. The plot of the calculated curve against the experimental points shows a dramatic divergence for the highest concentration of Δ**2** (Δ**1**−Δ**2** in Figure 4), suggesting a second equilibrium processes. If the 1/2 model leads to more convincing fits, it is not adequate with the Job plots when it is considered as the unique stoichiometry of the pairing in solution. The coexistence of the two stoichiometries within a fast exchange dynamic is proposed.

The magnitude order of the association constants is fully consistent with an ion-pairing assisted by π-stacking via the aromatic rings of the partners **1** and **2**, Coulombic forces being too weak by themselves for such a binding. For comparison, Keene and co-worker[14] obtained values for K_1 in the range 50 to 130 M^{-1} depending upon the anion associated with $[Ru(Me_2bpy)_3]^{2+}$. In the latter systems, electrostatic factors are highly predominant to facilitate the association since the anions are aliphatic (octanoate) or aromatic limited to one ring (benzoate). In the present work, the K_1 values are at least from 15- (Λ**1**−Δ**2**) to 37- (Δ**1**−Δ**2**) fold higher and the error margins much lower.[15] When K' is considered, the gap increases (from 120- (Λ**1**−Δ**2**) to 260- (Δ**1**−Δ**2**) fold higher than the "best" K' value from a classical anion). Again, the obtained values are acceptable for species in which the aromatic rings are not widely extended. As a comparison, the self-association constant of $[Ru(bpy)_2(tpphz)]^{2+}$ with tpphz, the tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]phenazine, a heptacyclic aromatic ligand, is only ca. 2×10^2 M^{-1}.[16] This study highlights the predominant role of the π-stacking interactions when enhanced by the similar shape (propeller type) of the involved partners.

More importantly, the preference for the formation of a homochiral pairing, as opposed to heterochiral, emerges from the results of Table 2. This is in line with the reported works on the specific chiral recognition of Δ**2** to the Δ-$[Ru(4,4'\text{-}Me_2bpy)_3]^{2+}$ cation.[7b] In terms of geometry, the homochiral pairing maximizes the $\pi-\pi$ interactions since three bpy's of the Ru cation stack with three aromatic rings of the Trisphat anion. This overlap is reduced to one for the heterochiral pairing. Calculations show that the first equilibrium (K_1) is favored within the Δ**1**−Δ**2** assembly vs Λ**1**−Δ**2**, while the second equilibrium (K_2) is similarly reached for both assemblies. We feel that K_2 might increase with the concentration of the metallic species for the homochiral pairing.

Proposed Structural Geometry for the Ion-Pairing. In a recent work,[17] the fluorinated derivatives of Δ-Trisphat were synthesized in order to be suitable to the NMR investigation of the ion-pairing. By means of 1D ^1H and ^{19}F NMR spectra completed with 2D $^1H/^{19}F$-HOESY NMR spectra, the topography within the preferred homochiral pairing (with Δ-$[Ru(4,4'\text{-}Me_2bpy)_3]^{2+}$ as cation) has been examined. Conclusions report that the homochiral associations of the mentioned D_3-symmetric salts result from organization of the propeller ions along the C_3 axes over C_2 axes.

In the present work, the anion is still D_3-symmetric while the cation is C_1. Moreover, the functionalized bpy ligand bears a Me and a COOH group capable of H-bonding. From the NMR spectral analyses, i.e., frequency shift, signal splitting, and line broadening, the structural geometry of the pairing may be depicted.

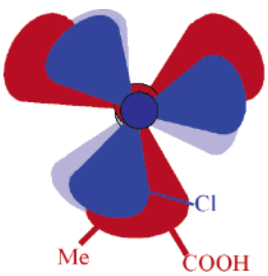

Figure 5. Schematic view of the Δ**2**−Δ**1**−Δ**2** ion pairing showing the stacking of the bpy ligand of **1** (red) with the halogenated rings of **2** (blue). The ring of Δ**2** stacking Hcmbpy twists toward the methylated pyridine of Hcmbpy.

For both Λ**1** and Δ**1** enantiomers, the protons of Hcmbpy undergo the greatest frequency shift as opposed to the bpy protons, in agreement with closer interionic contacts of Hcmbpy with **2**. The signal splitting within the whole spectra of Δ**1** gives clear evidence that the three bpy ligands interact with Δ**2**. This is not obvious for Λ**1**, for which the number of ^1H NMR signals mimics a D_3-pseudosymmetry edifice. Cartography of the impact of Δ**2** upon the Hcmbpy protons shows that the methylated ring is much more perturbed in contrast to the COOH ring. The preference of classical anions for methylated cations is reported by others,[14] but this trend is debated for the Trisphat family.[17] One is reminded that Δ**2** is highly lipophilic but also includes halogens that can participate in charge-assisted hydrogen bonds. We feel that the lipophilicity of Δ**2** orientates one of its halogenated rings toward the methylated part of Hcmbpy whether Λ**1** or Δ**1**. When Δ**1** is involved, the other halogenated rings closely stack with the two unsubsituted bpy. The organization of the propellers around a central axis through the P (Δ**2**) and Ru (Δ**1**) atoms as a pearl necklace with alternation of anion−cation−anion is retained for the homochiral assembly (Figure 5). The stacking becomes poor when the cation is Λ**1** since the two propellers (namely, Λ**1** and Δ**2**) are oppositely turned. In this case, the assembly is less organized.

Conclusion

The chiral ion-pairing of the cationic Δ- or Λ-$[Ru(bpy)_2(Hcmbpy)]^{2+}$ species to the anionic Δ-$Trisphat^-$ occurs as a fast exchange process in solution. This dynamic process exchanges the 1/1 stoichiometry with the 1/2 of the Ru−Trisphat pairing, as observed from Job's method. This result is unexpected if only the global charge of the two ions is considered, but is fully explained by the electronic delocalization over the full metal species via the metal-to-ligand charge transfer process completed by the π-conjugation within the bpy ligands. For the first time, the association constants for the Δ**1**−Δ**2** and Λ**1**−Δ**2** ion-pairings are quantified. The calculations give reliable and accurate values of K', which corresponds to the equilibrium associated with the 1/2 Ru/Trisphat stoichiometry. The magnitude order of K' is in agreement with Coulombic attractions assisted by a $\pi-\pi$ stacking between the bpy ligands of the cation and the aromatic rings of the anion. More importantly, the homochiral pairing Δ**1**−Δ**2** is favored as opposed to the heterochiral Λ**1**−Δ**2**, as outlined by the respective K' values ($K' = 4.46 \times 10^5$ and 2.05×10^5 M^{-2}). Further, in the homochiral ion pair, the cationic and anionic propellers adequately fit to maximize the π-stacking interactions even when the symmetries are C_1 and D_3, respectively.

A schematic view of the Δ**2**−Δ**1**−Δ**2** association for 1/2 Ru/Trisphat stoichiometry illustrates this supramolecular structure.

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(15) Keene et al. mention that the errors in their values are ±50%, which could question the 1/2 model for their ionic systems. As no stoichiometry determination is reported, we suspect that the model has been chosen on the a priori charges stoichiometry.

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Experimental Section

General Procedures. ^{1}H NMR spectra were obtained on Bruker DRX-500 and DMX-500 spectrometers with a 5 mm Z-gradient inverse probe at 283 K. ^{1}H NMR experiments were carried out in the CD_2Cl_2/CD_3CN, 90/10, solvent mixture with the residual $CDHCl_2$ signal as internal standard (at 5.32 ppm). Partial suppression of the $CDHCl_2$ peak was accomplished by presaturation.

Each spectrum was obtained with 360 scans, 5000 Hz sweep width, 32 K points, 3.75 μs (30°) pulse, and 2 s repetition time. Prior to FT, a 0.3 Hz exponential line broadening was applied to the FID.

Materials. All solvents used were reagent grade or better. The complexes $[Ru(bpy)_2(Hcmbpy)]^{2+}$ were prepared according to literature procedures.[6,8] The absolute configurations (Δ and Λ) were assigned by circular dichroism (CD). The CD spectra recorded in acetonitrile were compared to those previously reported.[8] Δ-Trisphat (Δ-tris(tetrachlorobenzenediolato)phosphate(V)) was synthesized according to the procedure previously described[18] and obtained as the $N(Bu)_4^+$ salt. Deuterated solvents were used as received. For the preparation of the NMR samples, the solvents, products, and glassware were deposited in a cool room (4 °C) 1 h before their utilization for the thermal equilibration.

Diffusion Measurements. Experiments were performed for Δ**1** at 0.3 and 9 mM (monomeric molar concentration) at a set temperature of 283 K. The Δ**1** enantiomer was chosen for the diffusion investigation, as it is the best "candidate" for pairing to the Δ-Trisphat, the assumption of similar aggregation level for both Δ**1** and Λ**1** being realistic. The measurements were carried out using a bipolar pulse pair longitudinal eddy current delay (BPP-LED) pulse sequence,[19] an improved version of the basic gradient echo (PFG) sequence.[20] The gradient shape was rectangular with a length (δ) of 2.0 ms. The gradient strength (G) was incremented from 5 to 50% of the maximum gradient strength ($G_{max} = 0.435$ T/m) in steps of 1, 2, and 5% to generate a 20-point set. The diffusion delay Δ (delay between the midpoints of the gradients) was set at 105 ms, and the recovery delay τ at 500 μs. The number of scans per increment was 32 or 256 depending on the concentration, and the relaxation delay was 10 s. Typical total experimental times were 2 and 20 h for the sample at 9 and 0.3 mM, respectively. Cation diffusion rates (D) were measured using the H3 and Me (Hcmbpy ligand) ^{1}H signals, as these peaks are well separated from others in the spectrum and were compared with that from the residual $CHDCl_2$ solvent signal. D values were determined from the curves giving the signal intensity ($I(f)$ au) vs G^2 (with $G = fG_{max}$) according to eq 1.

$$I(f) = I_0 e^{-(\gamma \delta f G_{max})^2(\Delta - \delta/3 - \tau/2)D} \qquad (1)$$

where $I(f)$ is the observed signal intensity as a function of a fraction (f) of the maximum gradient strength (G_{max}), I_0 is the signal intensity without gradient, and γ is the gyromagnetic ratio of the observed nucleus. Theoretical curves were generated using the DOSY analysis module within NMRPipe, implemented on Silicon Graphics stations.

Stoichiometry Determination. Job's Plot. Stoichiometry of the Λ**1**−Δ**2** and Δ**1**−Δ**2** pairings was determined using Job's method of continuous variation.[11] The sum of the initial concentrations $[\mathbf{1}]_0 + [\mathbf{2}]_0$ was held to 2.5 mM (with $\mathbf{1} = \Lambda\mathbf{1}$ or $\Delta\mathbf{1}$). The individual concentrations $[\mathbf{1}]_0$ and $[\mathbf{2}]_0$ were varied to yield mole fractions from 0 to 1 in increments of 0.1, while the final volume (500 μL per NMR tube) remained constant along the series. Typically, stock solutions of Λ**1** or Δ**1** and Δ**2** (2.5 mM) were prepared by accurately weighing out known amounts of the dried compounds and dissolving them in the deuterated solvent mixture. Three milliliters of each stock solution were thus prepared in a cool place by means of a microsyringe in order to prevent the evaporation of CD_2Cl_2. Eleven NMR samples were obtained by mixing different appropriate volumes of Λ**1** or Δ**1** with Δ**2**. The plot of $\Delta\delta_1[\mathbf{1}]_0$ against the molar ratio, $x = [\mathbf{1}]_0/([\mathbf{1}]_0 + [\mathbf{2}]_0)$, was built up for each Ru enantiomer. $\Delta\delta_1$ is the frequency shift of Λ**1** (or Δ**1**) in presence of Δ**2** relative to Λ**1** (or Δ**1**) alone. The Job curves present a maximum from which the **1**-to-**2** stoichiometry is determined and zero values at $x = 0$ and $x = 1$.

Titration. Six milliliters of stock solutions of Λ**1** and Δ**1** (0.3 mM) were prepared by accurately weighing out known amounts of the dried compounds and dissolving them in the CD_2Cl_2/CD_3CN, 90/10, mixture at cool temperature. In parallel, a mother solution of Δ**2** (50.0 mM) in cool CH_2Cl_2 (1 mL) was prepared. Eighty microliters of the mother solution was utilized to obtain a first dilution at 5.0 mM and a second one at 0.5 mM. Ten eppendorf vials containing Δ**2**, with $[\mathbf{2}] = 50.0$, 20.0, 10.0, 7.0, 5.0, 2.0, 1.0, 0.7, 0.4, and 0.2 mM, were prepared from the mother solution or the appropriate dilution (additional aliquots of CH_2Cl_2 are necessary, 50.0 and 5.0 mM tubes excepted), and the solvent was allowed to completely evaporate at room temperature. Finally, 500 μL of the Λ**1** or Δ**1** solution was injected into each eppendorf, and the mixture stirred and transferred into the NMR tubes at cool temperature.

Calculation of Association Constants. The general-purpose computer program WinEQNMR optimizes association constants and the chemical shifts of the free and associated species within the different stoichiometries. The R-factor defined below is usually considered as the criterion of goodness-of-fit.

$$R = 100\left(\sum W_i(\delta_{obs} - \delta_{calc})^2 / \sum W_i(\delta_{obs})^2\right)^{1/2}$$

$W_i = 1$ for all points, δ_{obs} is the experimentally measured chemical shift of a selected proton, and δ_{calc} is the optimized chemical shift of the proton after data fitting.

For the binary system (1/1 Ru/trisphat), $\delta_{obs} = \delta_{\mathbf{1}}\chi_{\mathbf{1}} + \delta_{\mathbf{1-2}}\chi_{\mathbf{1-2}}$; $\chi_{\mathbf{1}} + \chi_{\mathbf{1-2}} = 1$ ($\chi_{\mathbf{1}}$ and $\chi_{\mathbf{1-2}}$ are the molar fractions of **1** and **1**−**2**, respectively; $\delta_{\mathbf{1}}$ and $\delta_{\mathbf{1-2}}$ refer to the same proton in the free Ru and in the **1**−**2** complex, respectively); δ_{calc} is optimized for **1** and for **1**−**2**.

For the ternary system (1/2 Ru/trisphat), $\delta_{obs} = \delta_{\mathbf{1}}\chi_{\mathbf{1}} + \delta_{\mathbf{1-2}}\chi_{\mathbf{1-2}} + \delta_{\mathbf{2-1-2}}\chi_{\mathbf{2-1-2}}$; $\chi_{\mathbf{1}} + \chi_{\mathbf{1-2}} + \chi_{\mathbf{2-1-2}} = 1$ ($\chi_{\mathbf{2-1-2}}$ is the molar fraction of **2**−**1**−**2**; $\delta_{\mathbf{2-1-2}}$ the chemical shift of the selected proton in the **2**−**1**−**2** complex); δ_{calc} is optimized for **1**, **1**−**2**, and **2**−**1**−**2**.

Supporting Information Available: The diffusion data for Δ**1** are determined from the plots of I (signal intensity given in arbitrary units) as a function of G^2 (with $G = fG_{max}$ in T/m) for the selected H3 and Me signals and for the residual $CHDCl_2$ solvent signal. Experimental data (open circles) and fitted curves (lines) according to eq 1 are plotted at 9 mM (SMdif). Results are similar at 0.3 mM (data not shown). The WinEQNMR ouput files containing the raw data together with fitted parameters are provided for both Λ**1**−Δ**2** and Δ**1**−Δ**2** pairings and for the two studied stoichiometries (4 files, SM1: Λ**1**−Δ**2** in the 1/1 stoichiometry, SM2: Λ**1**−Δ**2** in the 1/2 stoichiometry, SM3: Δ**1**−Δ**2** in the 1/1 stoichiometry, SM4: Δ**1**−Δ**2** in the 1/2 stoichiometry). This material is available free of charge via the Internet at http://pubs.acs.org.

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