

Resolution of Conformationally Chiral mer -[Ru(dqp)₂]²⁺ and Crystallographic Analysis of [δ,δ -Ru(dqp)₂][Δ -TRISPHAT]₂ (dqp = 2,6-Di(quinolin-8-yl)pyridine; TRISPHAT = Tris(tetrachlorocatecholate)phosphate)

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The chirality of mono- or multinuclear ruthenium(II)-polypyridyl derivatives often plays a significant role in the characterization and use for various applications.^[1–5] The most common motif is [Ru(bpy)₃]²⁺, which is chiral (*D*₃ symmetry, Δ and Λ enantiomers) due to the disposition of the three bidentate 2,2'-bipyridine (bpy) ligands around the central Ru^{II} ion.^[6] We recently introduced a new class of conformationally chiral bistridentate Ru^{II} complexes with *D*₂ symmetry based on 2,6-di(quinolin-8-yl)pyridine (dqp) ligands, mer -[Ru(dqp)₂]²⁺ (**1**²⁺).^[7–10] As a consequence of all six-membered chelates, the dqp ligands adopt nonplanar helical conformations. The conformation of one ligand pre-determines the conformation of the second ligand (either λ,λ or δ,δ enantiomers) leading to intramolecular π -stacking between quinoline pairs.^[8] This is in contrast to typical bistridentate complexes based on planar 2,2':6',2''-terpyridine (tpy), which have *D*_{2d} symmetry and are thus achiral (Figure 1).

Complex **1**²⁺ is luminescent and exhibits an unusually long metal-to-ligand charge-transfer (MLCT), excited-state lifetime for a bistridentate Ru^{II} complex (3 μ s).^[11] This is even longer than for most trisbidentate Ru^{II} derivatives,^[12] which makes [Ru(dqp)₂]²⁺ complexes ideal candidates as photosensitizers for various light applications.^[13] It was debatable, however, if the two enantiomers interconvert in solution. Such interconversion must involve rotations about four biaryl bonds, two for each ligand, with concomitant dis-

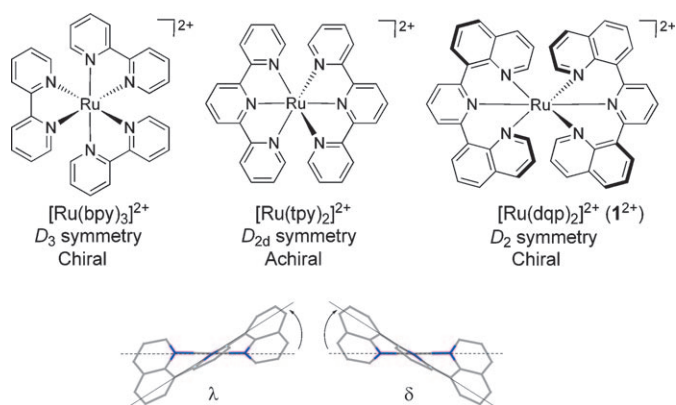


Figure 1. Top: Structures of [Ru(bpy)₃]²⁺, [Ru(tpy)₂]²⁺, and [Ru(dqp)₂]²⁺ (**1**²⁺). Bottom: Helical conformation of the dqp ligand. Illustration based on the X-ray crystal structure of **1**·[PF₆]₂ (one dqp ligand in each structure omitted for clarity).^[7]

ruption of the π -stacking interactions. Understanding these processes is a prerequisite if [Ru(dqp)₂]²⁺-based complexes are to be used, for example, for supramolecular or multinuclear complexes of well-defined structure and geometry. We therefore set out to explore the configurational stability of **1**²⁺, the first results which are presented herein.

To probe the chirality of **1**²⁺, the chiral TRISPHAT anion (TRISPHAT = tris(tetrachlorocatecholate)phosphate(V)) introduced by Lacour^[14,15] was selected as auxiliary. This ion has been used to evidence chirality in a wide range of cationic molecules with either central, axial, planar, or helical chirality.^[15] It has been particularly useful as resolving agent^[16–20] and NMR chiral shift reagent^[17–24] for configurationally stable trisbidentate Ru^{II} complexes. Upon association of racemic Ru^{II} complexes with enantiomerically pure [TRISPHAT][−] counterions, diastereomeric ion pairs are formed that may be separated by selective precipitation, asymmetric extraction, or chromatography.^[15] In contrast, in

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association with configurationally labile metal complexes, such as trisbidentate Fe^{II} derivatives,^[25,26] equilibration may occur with the formation of one predominant configuration of the diastereomeric ion pairs (Pfeiffer effect).^[27]

The racemic **1**-[PF₆]₂ was prepared by following the original procedure reacting the dqp ligand (2 equiv) with [Ru(dmsO)₄Cl₂] in refluxing ethylene glycol.^[7] The high temperature ensures the formation of the thermodynamically favored *mer*-isomer instead of the kinetically favored *fac*-isomers.^[10] The ¹H NMR of **1**-[PF₆]₂ has previously been described in some detail in CD₃CN.^[8] To promote asymmetric ion pairing with enantiomerically pure [Δ-TRISPHAT]⁻, the ¹H NMR experiments in this study were performed in CD₂Cl₂. The spectrum of **1**-[PF₆]₂ shows eight well-separated signals in accordance with the high symmetry of the complex (Figure 2A). Addition of one equivalent of [Bu₄N][Δ-

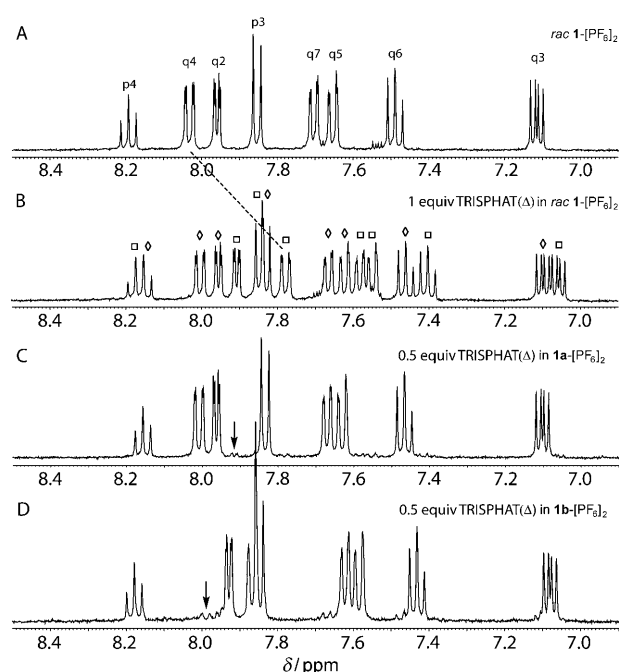
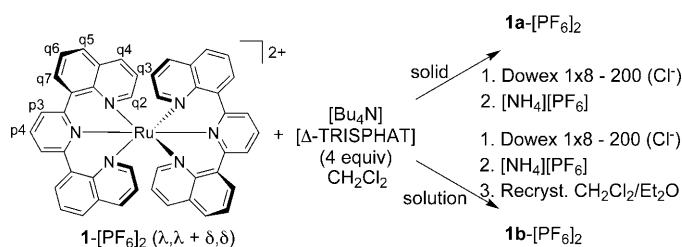


Figure 2. A: ¹H NMR of racemic **1**-[PF₆]₂ in CD₂Cl₂ ([Ru]=3.3 mM). B: After addition of 1 equivalent of [Bu₄N][Δ-TRISPHAT]. □ and ◇ are the two ion pairs. C: **1a**-[PF₆]₂ and 0.5 equivalents of [Bu₄N][Δ-TRISPHAT] ([Ru]=2.0 mM). D: **1b**-[PF₆]₂ and 0.5 equivalents of [Bu₄N][Δ-TRISPHAT] ([Ru]=2.0 mM). Arrows in C/D indicate the other ion pair.

TRISPHAT] to the racemic mixture in CD₂Cl₂ resulted in a splitting of the ¹H signals in a 1:1 ratio attributed to two diastereomeric ion pairs (Figure 2B). This is consistent to numerous reports on the use of [TRISPHAT]⁻ as NMR chiral shift reagent for Ru^{II} trisbidentate complexes.^[17–24] As seen in Figure 2B, good separation (Δδ), in general 0.05–0.1 ppm, is observed for all protons. The largest Δδ is for H^{q4}, which is shifted upfield by approximately 0.3 ppm for one ion pair. Upon further addition of [Δ-TRISPHAT]⁻ (in total 2 equiv), a decrease in one set of signals appeared and with a concomitant formation of a solid in the NMR tube (Figure S1 in the Supporting Information). Rather than being an

equilibration favoring one of the diastereomeric ion pairs, it therefore indicated selective precipitation of one of the ion pairs. Further addition of [Δ-TRISPHAT]⁻ (in total 4 equiv) showed almost complete loss of one set of signals. It is interesting to note that the ion pair that exhibits the most pronounced chemical shift difference, indicating strong ion pair interactions,^[23,28] remains in solution (Figure S1 in the Supporting Information).

The ESI-MS of the redissolved precipitate showed a mono-charged MS peak at *m/z* 1536 corresponding to the **1**-[Δ-TRISPHAT]⁺ ion (Figure S2 in the Supporting Information). Initial attempts to perform anion metathesis on silica gel using saturated [NH₄][PF₆] in CH₃CN as described by Brodie and Aldrich-Wright^[29] were unsuccessful. Only signals attributed to [Δ-TRISPHAT]⁻ were observed by ³¹P NMR spectroscopy of the recovered solid. Instead, the precipitate (**1a**-[Δ-TRISPHAT]₂) was converted to the PF₆⁻ salt in 43% yield by using Dowex Cl⁻ exchange resin followed by precipitation with [NH₄][PF₆] (Scheme 1). The re-



Scheme 1. Resolution of **1**²⁺ and subsequent isolation as PF₆⁻ salts.

maining complex in the filtrate (**1b**²⁺) was isolated as the PF₆⁻ salt in 44% yield using a similar protocol as for **1a**-[PF₆]₂. Additional recrystallizations were needed, however, to remove excess ammonium salts. The similar isolated yields of **1a**-[PF₆]₂ and **1b**-[PF₆]₂ supports the fact that conformational equilibration is not occurring during the selective precipitation of one diastereomeric ion pair.

To further address the configurational stability and to determine the stereoselectivity of the precipitation, the ¹H NMR spectra of complexes **1a**²⁺ and **1b**²⁺ were studied in more detail. The spectra of **1a**-[PF₆]₂ and **1b**-[PF₆]₂ in CD₂Cl₂ after addition of 0.5 equivalents of [Δ-TRISPHAT]⁻ are shown in Figure 2C and 2D. Careful control of Ru concentration was necessary to avoid precipitation of **1a**-[Δ-TRISPHAT]₂ as discussed above. At a concentration of [Ru]=2.0 mM and only 0.5 equivalents [Δ-TRISPHAT]⁻ clear differences in chemical shifts for the ion pairs occur, while no precipitation was observed. The chemical shifts are expected to be a function of the Ru²⁺/[Δ-TRISPHAT]⁻ ratio,^[23] and small variations are also observed comparing with the racemic sample in Figure 2B. This is most evident for H^{q4} in **1b**²⁺ (Figure 2D), which show a smaller induced shift at the lower [Δ-TRISPHAT]⁻ concentration (≈0.2 ppm). In case of **1a**²⁺ (Figure 2C), the signals of the diastereomeric ion pair is almost lost in the baseline noise, and the enantiomeric excess of **1a**-[PF₆]₂ is ≥95%. As ex-

pected, for the enantiomer **1b**-[PF₆]₂, which remained in solution, the purity is somewhat lower (*ee* ≥ 90%). Importantly, no change in relative intensity was observed in either of the samples over time demonstrating the configurational stability of the samples. Even after heating **1a**-[PF₆]₂ in CH₃CN at 80 °C for one hour, the ¹H NMR spectrum after addition of [Δ-TRISPHAT][−] was identical to that shown in Figure 2C, showing that no racemization occurs during these conditions. Similarly, no racemization was observed when **1a**-[PF₆]₂ was irradiated with visible light for 30 min in CD₂Cl₂.

The absolute configuration of **1a**²⁺ was determined by X-ray analysis of **1a**-[Δ-TRISPHAT]₂ (see Experimental Section). The structure determination showed the helical arrangement of the dqp ligands with δ,δ absolute configuration (Figure 3). Intramolecular π-stacking interactions be-

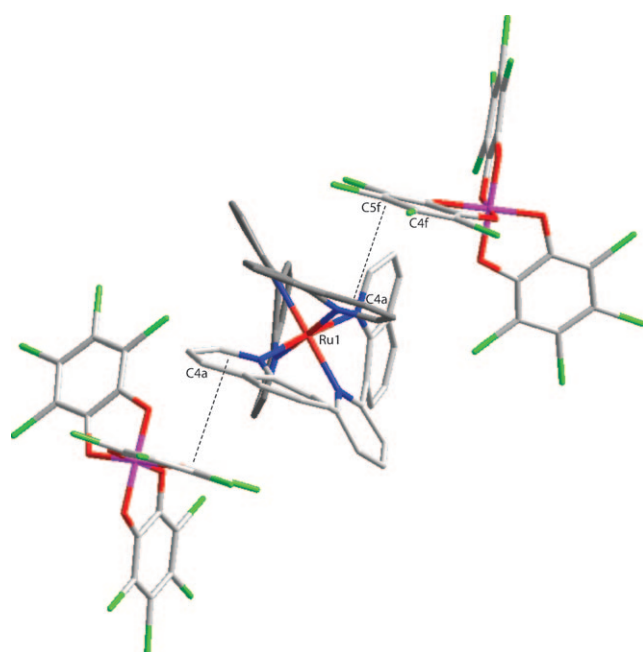


Figure 3. X-ray diffraction analysis of **1a**-[Δ-TRISPHAT]₂ illustrating the helical conformations of the dqp ligands with δ,δ configuration, and the intermolecular π-stacking interactions between the quinolines and one tetrachlorocatecholate moiety. C4a–C4f ≈ 3.45 Å, C4a–C5f ≈ 3.55 Å. H atoms have been omitted for clarity.

tween quinoline pairs are evident, and the Ru–N bond lengths (2.032(5)–93(6) Å) and N–Ru–N bite angles (177.2(2)°) are similar to those previously observed for **1**-[PF₆]₂.^[7,9] Several intermolecular close contacts are observed in the solid state for **1a**-[Δ-TRISPHAT]₂. The C4a–C4f and C4a–C5f distances between each quinoline and one tetrachlorocatecholate moiety of [Δ-TRISPHAT][−] are ≈ 3.45 and 3.55 Å respectively, suggesting π-stacking interactions (Figure 3). Other close contacts include C–H⋯Cl, C–H⋯π, and C–Cl⋯π (Figure S3 in the Supporting Information). Although no strong interactions were observed by ¹H NMR spectroscopy in solution, the crystal packing forces are evi-

dently favored for **1a**-[Δ-TRISPHAT]₂ leading to the selective precipitation of this ion pair.

The CD spectra for **1a**-[PF₆]₂ and **1b**-[PF₆]₂ were recorded in CH₃CN at a concentration of ≈ 2.5 × 10^{−5} M (Figure 4).^[30] As expected, there is a mirror-image relationship illustrating the enantiomeric relationship between the two complexes. Consistent with the NMR data, no change in CD signal was observed over time demonstrating their configurational stability.

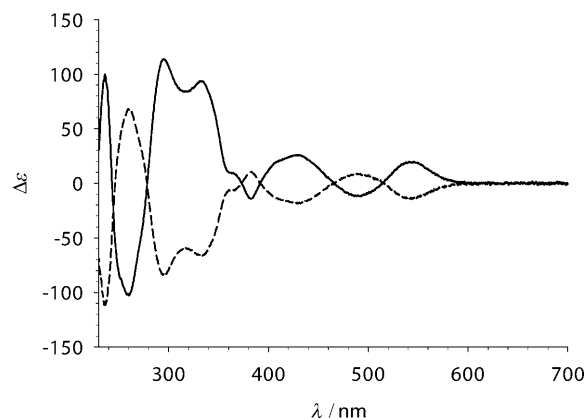


Figure 4. CD spectra of **1a**-[PF₆]₂ (solid line) and **1b**-[PF₆]₂ (dashed line) in CH₃CN.

In conclusion, we have demonstrated that chiral [Ru(dqp)₂]²⁺ (**1**²⁺) is configurationally stable and may be resolved by selective precipitation of one diastereomeric ion pair. The chirality of **1**²⁺ results from the helical conformations of the dqp ligands and may be viewed as a form of atropisomerism.^[31] Given the favorable photophysical properties of this class of Ru^{II}-polypyridyl complexes, it is of prime interest to understand their structural features for further use for other applications. Current investigations focus on the role of the intramolecular π-stacking between quinoline pairs on the configurational stability.

Experimental Section

Resolution of *rac*-[Ru(dqp)₂][PF₆]₂ (1**-[PF₆]₂):** [Bu₄N][Δ-TRISPHAT] (0.057 g, 0.056 mmol, 4 equiv) was added to a solution of **1**-[PF₆]₂ (0.015 g, 0.014 mmol) in CH₂Cl₂ (4.0 mL) and the mixture was left for 30 min. The formed solid was collected and washed with additional CH₂Cl₂ and Et₂O. The solid was stirred in H₂O/CH₃CN (7:3) with a few drops of acetone in the presence of Dowex 1 × 8–200 (Cl[−]). When all dissolved, the mixture was filtered and **1a**-[PF₆]₂ (δ,δ) was precipitated by addition of aqueous [NH₄][PF₆]. The solid was collected by filtration and washed with H₂O and Et₂O (43%). Complex **1b**-[PF₆]₂ (λ,λ) was obtained in 44% isolated yield through the same procedure from the solution after [Δ-TRISPHAT][−] addition. Ion exchange using Dowex was performed twice to achieve complete removal of excess [Δ-TRISPHAT][−]. The obtained solid was further purified by two recrystallizations from CH₂Cl₂/Et₂O to remove [Bu₄N][PF₆]. ¹H NMR data for **1**-[PF₆]₂ (400 MHz, CD₂Cl₂, 25 °C, TMS): δ = 7.12 (dd, *J* = 8.4, 5.1 Hz, 4H), 7.49 (dd, *J* = 8.0, 7.3 Hz, 4H), 7.65 (dd, *J* = 8.4, 1.1 Hz, 4H), 7.70 (dd, *J* = 7.3,

1.1 Hz, 4H), 7.85 (d, $J=8.1$ Hz, 4H), 7.96 (dd, $J=5.1, 1.4$ Hz, 4H), 8.03 (dd, $J=8.1, 1.4$ Hz, 4H), 8.19 ppm (t, $J=8.1$ Hz, 2H).

X-ray crystallographic data for 1a-[Δ -TRISPHAT]₂: Single crystals were obtained by vapor diffusion (acetone/CH₃CN). RuN₆C₈₂H₃₀P₂O₁₂Cl₂₄, dark-red blocks, crystal dimension = 0.35 × 0.20 × 0.15 mm, tetragonal, $P4_2,2$ (No. 92), $a=15.7699(1)$, $c=37.7117(3)$ Å, $V=9378.51(11)$ Å³, $\rho_{\text{calcd}}=1.632$ g cm⁻³, $2\theta_{\text{max}}=44.3^\circ$, $\text{MoK}\alpha$ ($\lambda=0.71073$ Å), ω -scans at different ϕ to fill Ewald sphere, room temperature (291 K), measured reflections = 60658, unique reflections = 5556, observation limit: $I \geq 2\sigma(I)$, total number of parameters = 573. Lorentz, polarization and empirical absorption correction (multiscan) applied by diffractometer software (CrysAlis), with relative transmission limits $T_{\text{min}}=0.889$, $T_{\text{max}}=1.000$. Structure solved using traditional direct methods with SHELXS and refined with full-matrix least-square calculations on F^2 using SHELXL.^[32] Hydrogen atoms refined in riding mode, $R=0.0533$, $wR2=0.1530$. Minimum and maximum residual densities = -0.703, 0.815. The refined Flack parameter = 0.01(6) indicates correct absolute configuration. CCDC-764015 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: chiral resolution • conformational isomerism • N ligands • ruthenium

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