Comparison of the NMR enantiodifferentiation of a chiral ruthenium(II) complex of C_2 symmetry using the TRISPHAT anion and a lanthanide shift reagent

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Received (in London, UK) 18th November 2002, Accepted 24th February 2003
First published as an Advance Article on the web 6th March 2003

The tris[tetrachlorobenzenediolato]phosphate(V) anion (TRISPHAT) is known to be an efficient NMR chiral shift agent for various chiral cationic species. Here we compare the efficiency of TRISPHAT and of a chiral lanthanide shift reagent for the determination of the enantiomeric purity of the chiral building block $[Ru(phen)_2py_2]^{2+}$ which possesses C_2 symmetry. We also discuss our results in terms of the geometry of interaction between the Ru(II) complex and the TRISPHAT anion.

Introduction

Polyazaaromatic Ru(II) complexes have been studied for a number of years. They represent important molecular targets not only for the study of fundamental processes such as energy and electron transfer[1] but also for the development of applications in organic light emitting diodes,[2] photoelectrochemical cells,[3] biological and medical diagnostics and phototherapy.[4] In several of these different areas, the need to use pure enantiomers has been clearly demonstrated. The resolution of these complexes has thus become of prime importance. Different synthetic strategies have been developed in order to achieve this goal. They are based either on the use of chiral ligands that induce the formation of a metal centre of one configuration exclusively (Δ or Λ), or of enantiopure precursors which possess in a *cis* position two monodentate ligands which are sufficiently labile to be substituted with retention of configuration by a bidentate ligand.[5] $[Ru(phen)_2py_2]Cl_2$ is such a precursor and its two enantiomers can be resolved by diastereoisomeric crystallization with an enantiomer of arsenyl tartrate.[6] Solid state interactions between $[Ru(phen)_2py_2]^{2+}$ and chiral anions (dibenzoyl tartrate) have been described.[7] However, to our knowledge, no such solution studies have been reported.

NMR spectroscopy in the presence of chiral shift reagents is a particularly well-adapted technique for determining the enantiomeric purity of chiral molecules.[8] Its advantage over chiro-optical methods is that there is no need to be in possession of parameters which characterize the pure enantiomers. The NMR method simply requires the use of a chiral auxiliary that converts the mixture of enantiomers into a mixture of diastereoisomeric complexes. As soon as there is a large enough chemical shift non-equivalence to give baseline resolution between the signals of analogous nuclei in these diastereoisomeric complexes, integration yields a direct measurement of the enantiomeric purity.

Chiral lanthanide shift reagents, such as europium derivatives, have been used since the 1970s as chiral auxiliaries.[8] They form, *via* interaction with electron donor sites, a weak addition complex with a large variety of compounds. The induced pseudo-contact shifts are a function of the distance between the nuclei under observation and the lanthanide center and are in general quite large (of the order of several ppm).[9] The addition complex is in fast exchange on the NMR chemical shift time scale with the unassociated compound. The observed signals are generally large and devoid of any fine structure due to the fact that under fast exchange conditions, line broadening is proportional to the square of the difference in shifts.[10]

Barton and Nowick[11] were the first to report the use of chiral lanthanide shift reagents for the determination of the enantiomeric purity of Ru(II) cationic complexes. They undertook their study with $[Ru(phen)_3]^{2+}$ and observed that both the nature of the Ru(II) counterion and the polarity of the solvent influence the degree of induced shift. They explain their observations by the fact that the lanthanide shift reagent interacts not with the Ru(II) dication, which does not possess any electron donor sites, but with its counterions; small highly charged anions and solvents of low polarity lead to a better interaction between the lanthanide shift reagent and the Ru(II) dication. The observed signals were relatively broad but the spectra could be assigned without ambiguity since they exhibit few resonances (4 for each enantiomer). The relatively low solubility of the Ru(II) complex in the chosen solvent of low polarity, CD_2Cl_2, and the induced line broadening meant that Barton *et al.* could only detect the minor isomer when it was present at a molar fraction greater than 0.1.

Several other groups have reported the use of chiral lanthanide shift reagents in the estimation of the enantiomeric purity of Ru(II) cationic complexes.[12,13] When the ligands of the Ru(II) complexes possess electron donor sites it has been observed that it is possible to work in more polar solvents (CD_3CN and CD_3OH) since ion-pair formation is no longer crucial.[13] Increased amounts of europium shift reagent are however necessary in order to obtain a clear separation of analogous peaks due to competition with the solvent molecules

 DOI: 10.1039/b211419d

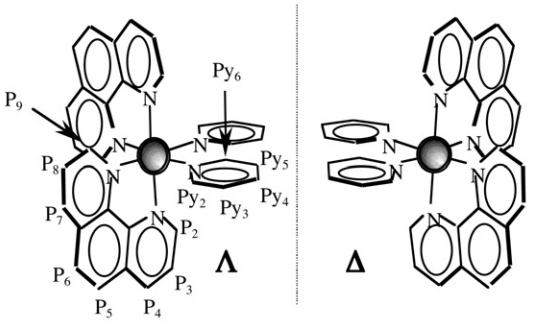

Fig. 1 The two enantiomers of $[Ru(phen)_2py_2]^{2+}$ and atom labelling.

which possess electron donor sites. In all cases, excessive line broadening and distorted baselines complicate the quantitative analysis.

Recently, the tris[tetrachlorobenzenediolato]phosphate(v) anion, known as TRISPHAT, has been shown to be an excellent diamagnetic NMR chiral shift reagent, which can be used to determine the enantiomeric purity of various chiral cationic species including metal complexes.[14–19] The Λ enantiomer is isolated as the tri-*n*-butylammonium salt, $[Bu_3NH][\Lambda$-TRISPHAT], which is soluble in pure $CDCl_3$ and CD_2Cl_2. The Δ-enantiomer is prepared as the cinchonidinium derivative, which is only soluble in polar solvent mixtures ($>7.5\%$ DMSO in $CDCl_3$). This latter compound can however be transformed into the tetraethylammonium salt, $[Et_4N][\Delta$-TRISPHAT], which readily solubilizes in non-polar solvents.

The TRISPHAT anion forms diastereoisomeric contact pairs directly with chiral cations and the short-range interactions lead to a large non-equivalence and clear differences in the NMR spectra of the two diastereoisomeric ion-pairs. The polarity of the solvent influences the quality of the separation since ion association is crucial. Exchange is fast on the NMR chemical shift time scale but the signals are not substantially broadened.

Here we present the results of a study undertaken with the chiral building block of C_2 symmetry $[Ru(phen)_2py_2]^{2+}$ (Fig. 1). We compare the efficiency of TRISPHAT and of a chiral lanthanide shift reagent for the determination of its enantiomeric purity. Such a systematic comparison has, interestingly enough, never been reported in the literature. We also present results which we discuss in terms of geometries of interaction between the Ru(II) complex and the TRISPHAT anion.

Results and discussion

The ^1H NMR spectrum of $[Ru(phen)_2py_2]Cl_2$ in CD_2Cl_2 exhibits 11 signals corresponding to the 8 non-equivalent protons on the phenanthroline rings and to the 3 groups of chemically non-equivalent protons on the pyridine rings (Fig. 2a). The fact that the homologous protons on the two phenanthroline rings and the two pyridines are chemically equivalent indicates that the pyridine rings rotate freely which confers a C_2 symmetry to the complex. Figs. 2(b) and 2(c) are spectra of *rac*-$[Ru(phen)_2py_2]Cl_2$ recorded in CD_2Cl_2 in the presence of approximately one equivalent of $[Et_4N][\Delta$-TRISPHAT] and $[Bu_3NH][\Lambda$-TRISPHAT] respectively. Spectra 2(d) and 2(e) are the spectra of the resolved enantiomers of $[Ru(phen)_2py_2]Cl_2$ in the presence of approximately 1 equivalent of $[Bu_3NH][\Lambda$-TRISPHAT]. 11 signals are observed for each Ru(II) enantiomer in the presence of TRISPHAT indicating that the Ru(II) complex maintains its C_2 symmetry and that exchange is fast on the NMR chemical shift time scale.

The signals in all the spectra shown in Fig. 2 retain a fine-structure. Differences are however observed in the chemical

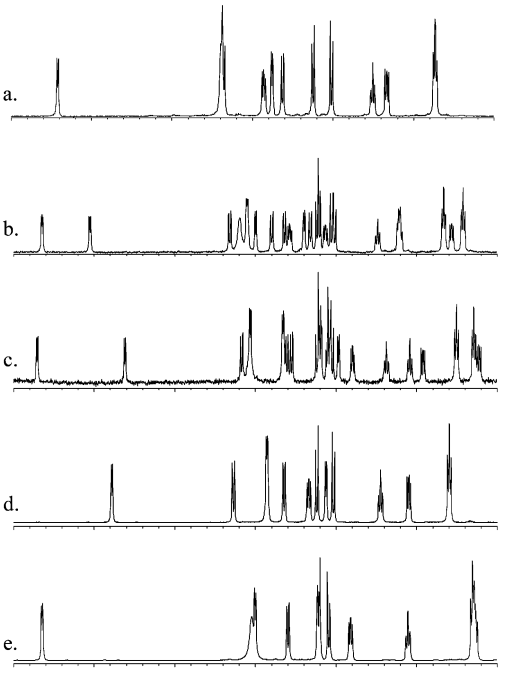

Fig. 2 (a) *rac*-$[Ru(phen)_2py_2]Cl_2$ without any TRISPHAT; (b) *rac*-$[Ru(phen)_2py_2]Cl_2$ with approximately 1 equivalent of $[Et_4N][\Delta$-TRISPHAT]; (c) *rac*-$[Ru(phen)_2py_2]Cl_2$ with approximately 1 equivalent $[Bu_3NH][\Lambda$-TRISPHAT]; (d) $[\Delta$-$Ru(phen)_2py_2]Cl_2$ with approximately 1 equivalent of $[Bu_3NH][\Lambda$-TRISPHAT]; (e) $[\Lambda$-$Ru(phen)_2py_2]Cl_2$ with approximately 1 equivalent of $[Bu_3NH][\Lambda$-TRISPHAT]; all spectra recorded in CD_2Cl_2 at 25 °C.

shifts in the different spectra. This is due to the fact that the system under study is very complicated and various ion associations can occur, each having a weighted contribution to the observed chemical shifts. The Ru(II) dication can associate with both monovalent anions present in solution (Cl^- and TRISPHAT) and these anions can also associate with the original TRISPHAT counterion ($[Bu_3NH]^+$ or $[Et_4N]^+$, depending on the TRISPHAT enantiomer used). The fact that the amount of TRISPHAT anions added cannot compensate all positive charges from Ru(II) dications and that mixed salts are present in solution does not simplify the problem. The chemical shifts are a function of the TRISPHAT/Ru(II) ratio in solution, and it was extremely difficult to control this ratio since $[Ru(phen)_2py_2]Cl_2$ is poorly soluble in CD_2Cl_2 and certain solutions had to be filtered before addition of the TRISPHAT salts. This particular solvent of low polarity was chosen because, as mentioned in the introduction, it is important to favour ion associations. It is worth noting that a good separation between certain analogous signals is already observed with the addition of approximately 0.1 equivalent of the TRISPHAT salts. No splitting of the signals is however observed when working in a more polar solvent, like CD_3CN, even with 2 equivalents of TRISPHAT.

It is also possible that a difference in the affinity of TRISPHAT for the two enantiomers of the Ru(II) complex is responsible for the difference in the chemical shifts observed in the spectra of the resolved samples (Figs. 2(d) and 2(e)) compared to the spectrum of the racemic complex (Fig. 2(c)). It has indeed been reported that the homochiral associations between TRISPHAT and chiral metal complexes are thermodynamically more favorable.[16,19,20] This is based on the observations that when using a pure enantiomer of TRISPHAT a clear selectivity, with a preference for the homochiral association, is observed in the asymmetric synthesis[20] and extraction[16,19] of stable mononuclear metal complexes and also in the

configurational ordering of labile iron(II) tris(diimine) complexes.[18] If such a preference exists in the present case we would expect a larger induced shift in the spectra of the resolved samples than in the spectrum of the racemic sample where the enantiomers are in competition for the TRISPHAT ions. This is not the case but it cannot be excluded that differences in the TRISPHAT/Ru(II) ratio affect the results.

When the different spectra of *rac*-$[Ru(phen)_2py_2]Cl_2$ were recorded in the presence of the TRISPHAT salts certain signals were initially broader than others. This broadening was not systematically reproducible but always disappeared when the samples were left to equilibrate. It can therefore be excluded that the broadening is due to an impurity present in the samples. Spectra presented in this paper were all recorded after at least 1 hour of equilibration. This broadening is probably due to the poor solubility of the Ru(II) dication and to the presence of aggregates; a certain amount of time is needed to reach equilibrium concentrations. Since a clear separation of the signals of homologous protons is observed with both enantiomers of TRISPHAT, it is possible to obtain the enantiomeric purity of resolved $[Ru(phen)_2py_2]Cl_2$ samples with good precision. In the case of the resolved samples used to record spectra 2(d) and 2(e), the signals of the enantiomer present in the lower concentration are practically lost in the baseline noise of the spectra and it can therefore be estimated that the enantiomeric purities of these samples are greater than 98% (precision of the integration).

We determined the effect of 1 equivalent of the two TRISPHAT salts on the chemical shifts of the protons of the two enantiomers of $[Ru(phen)_2py_2]Cl_2$. The complete assignment of the ^1H spectra of *rac*-$[Ru(phen)_2py_2]Cl_2$ in the presence of $[Et_4N][\Delta$-TRISPHAT] and $[Bu_3NH][\Lambda$-TRISPHAT] was achieved using 2D DQF-COSY spectra. Results are reported in Table 1. Even if it is difficult to make quantitative comparisons between the values in the table (the counterions of the two enantiomers of the TRISPHAT anion are not the same and we cannot be certain that we have exactly the same number of equivalents of TRISPHAT in both samples) it is interesting to note that for the heterochiral pairs, ΛRu-ΔTRISPHAT and ΔRu-ΛTRISPHAT, all the resonances are shielded and the largest shifts are observed for protons P_2, P_3, $Py_{2,6}$ and P_7 while for the homochiral pairs, ΔRu-ΔTRISPHAT and ΛRu-ΛTRISPHAT, the protons P_2 and P_9 are deshielded and the largest shielded shifts are observed for protons P_3, P_4 and P_8. The deshielded protons in the homochiral associations are the protons adjacent to the ligating nitrogens or closest to the axis of symmetry of the molecule. Similar shielding and deshielding patterns have been observed for the protons on the ligands of Ru(II) and Fe(II) complexes of D_3 symmetry in interaction with TRISPHAT: only the protons closest to the axis of symmetry in the homochiral pairs are deshielded.[15,19] This has been reported as being consistent with an ion-pairing model with the cation and the TRISPHAT interacting along their C_3 axis which, in the case of the homochiral association, leads to a co-threefold embrace of the propeller shaped molecules and a cation/anion distance which is shorter than in the heterochiral association. It is therefore possible that this geometry of interaction is also favored in the homochiral association between TRISPHAT and the $[Ru(phen)_2py_2]^{2+}$ dication which has a C_2 symmetry. The highly directional electrostatic interactions certainly play a central role in the positioning of the anions and cations relative to each other but it must be remembered that the other non-bonded interactions, especially the London forces, are also important in the stabilisation of the ion associations. Indeed, the London interactions are, contrary to what is generally thought, often the dominant ones in molecular associations.[21] It would be extremely difficult to try and gain insight into the geometry of interaction between TRISPHAT and the Ru(II) dication solely on the basis of a chemical shift analysis. Furthermore, since the C_2 symmetry of the Ru(II) dication is maintained in the presence of TRISPHAT, the association is probably quite loose.

Spectra of *rac*-$[Ru(phen)_2py_2]Cl_2$ were also recorded with increasing amounts of the europium salt derivative, tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]Eu(III) (or $Eu(tfc)_3$). $Eu(tfc)_3$ cannot interact directly with the ligands coordinated to the metal center (no electron donor sites). In order to observe a good separation of analogous signals of the Ru(II) complex approximately 5 equivalents of $Eu(tfc)_3$ had to be added to the solutions leading to a relatively important line broadening and to poor signal to noise ratios. Fig. 3 shows part of the spectrum of a solution of *rac*-$[Ru(phen)_2py_2]Cl_2$ into which approximately 5 equivalents of $Eu(tfc)_3$ were added. The signals exhibit significant shifts but it was impossible to achieve complete assignment of the spectra. Even if certain signals are well separated from the rest (proton P_2 for example, indicated by the arrows) the excessive line broadening induced by the addition of $Eu(tfc)_3$ made, contrary to what is observed with TRISPHAT, the precise quantitative analysis of resolved samples impossible.

The present results clearly show the advantage of using TRISPHAT compared to $Eu(tfc)_3$ for the determination of the enantiomeric purity of $[Ru(phen)_2py_2]^{2+}$. The NMR signals of the two enantiomers are indeed clearly distinct, exhibit different shielding or deshielding effects and, most importantly, remain narrow in the presence of the chiral auxiliary. The elaboration of a method which permits the determination of the enantiomeric purity of this compound with precision is of prime interest because it is a remarkably good chiral building block for the synthesis of promising Ru(II) complexes.

Table 1 Assignments of the different protons of the two enantiomers of *rac*-$[Ru(phen)_2py_2]Cl_2$ in the absence and presence of approximately one equivalent of $[Bu_3NH][\Lambda$-TRISPHAT] or of $[Et_4N][\Delta$-TRISPHAT] (* indicates approximate values (±0.1 ppm); P_5 and P_6 could not be assigned without ambiguity). The shifts induced by the TRISPHAT salts are also indicated ($\Delta\delta$). TRISPHAT is abbreviated as TRIS

		Δ-Ru + Λ-TRIS		Λ-Ru + Λ-TRIS		Δ-Ru + Δ-TRIS		Λ-Ru + Δ-TRIS	
Proton	No TRIS	δ	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$
P_2	9.70	9.31	−0.39	9.85	0.15	9.85	0.15	9.41	−0.29
P_3	8.42	8.0*	≈−0.4	7.90	−0.52	7.97	−0.45	8.21	−0.21
P_4	8.67	8.59	−0.08	8.28	−0.39	8.32	−0.35	8.65	−0.02
P_5/P_6	8.01/8.13	8.0*/8.1*	≈0	8.0*/8.1*	≈0	8.0*/8.1*	≈0	8.0*/8.1*	≈0
P_7	8.31	7.99	−0.32	8.1*	≈−0.2	8.1*	≈−0.20	8.1*	≈−0.2
P_8	7.67	7.46	−0.21	7.1*	≈−0.6	7.2*	≈−0.50	7.6*	≈−0.1
P_9	8.36	8.30	−0.06	8.53	0.17	8.53	0.17	8.32	−0.04
$Py_{2,6}$	8.68	8.33	−0.35	8.5*	≈−0.2	8.57	−0.11	8.46	−0.22
$Py_{3,5}$	7.36	7.25	−0.11	7.2*	≈−0.2	7.2*	≈−0.2	7.31	−0.05
Py_4	7.76	7.69	−0.07	7.54	−0.22	7.6*	≈−0.2	7.73	−0.03

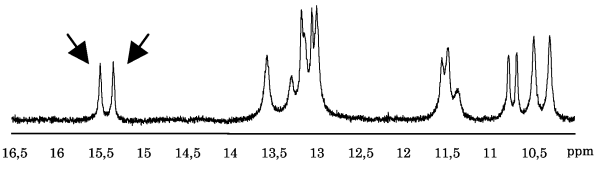

Fig. 3 ^{1}H NMR spectrum of *rac*-[Ru(phen)$_2$py$_2$]Cl$_2$ dissolved in CD_2Cl_2 with approximately 5 equivalent of Eu(tfc)$_3$. The arrows indicate the signals corresponding to proton P$_2$ (see Fig. 1 for numbering of the protons).

Materials and methods

[Ru(phen)$_2$py$_2$]Cl$_2$ was synthesized and resolved according to the methods described by Dwyer *et al.*[6] Tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]Eu(III) (or Eu(tfc)$_3$) was purchased from Aldrich Europe and used without further purification. CD_2Cl_2(99.6% D) and CD_3CN (99.8% D) were purchased from Euriso-top. The [Bu$_3$NH][Λ-TRISPHAT] salt was prepared following previously reported guidelines[14,22] and the [Et$_4$N][Δ-TRISPHAT] salt was prepared in a similar manner to [Bu$_4$N][Δ-TRISPHAT].[20,23]

Approximately 1 mM solutions of *rac*-, Δ- and Λ-[Ru(phen)$_2$py$_2$]Cl$_2$ were prepared in CD_2Cl_2. The solutions were filtered to remove any non-dissolved complex. Samples (800 μl) were placed in the NMR tubes. [Ru(phen)$_2$py$_2$]Cl$_2$ is known to undergo photodegradation in CD_2Cl_2 and the samples were therefore protected from light at all times. Concentrated stock solutions of Eu(tfc)$_3$, [Bu$_3$NH][Λ-TRISPHAT]and [Et$_4$N][Δ-TRISPHAT] were prepared in CD_2Cl_2. Their concentrations were calculated so that an injection of 10 μl of these solutions into the NMR tubes corresponds to an injection of approximately 0.1 equivalent of the shift reagent.

NMR spectra were recorded at 25 °C on a Varian Unity-600 spectrometer. One-dimensional spectra were recorded with acquisition times of 2 s and relaxation delays of 5 s. 128 scans were recorded in the absence of any shift reagent. At least 64 scans were recorded when TRISPHAT or Eu(tfc)$_3$ were used. Chemical shifts were referenced to residual solvent protons of CD_2Cl_2 resonating at 5.32 ppm relative to TMS. For the DQF-COSY spectra[24] 512 increments of 80 transients were recorded with an acquisition time of 0.188 s and a relaxation delay of 1 s. The spectral width was 6120 Hz in both dimensions and the digital resolution was 1.5 Hz/pt in F2 and 6 Hz/pt in F1.

Acknowledgements

The authors would like to acknowledge the Belgian FNRS (LEA CNRS-FNRS) and the "Communauté Française de Belgique" (ARC 2002–2007) for financial support. G.B., C.B. and F.P. thank the Belgian FRIA, the European TMR program (ERBFM-RXCT 980226) and the PAI 4 respectively for a fellowship. The authors would also like to thank David Monchaud, Jonathan Jodry and France Favarger for the preparation of the TRISPHAT salts and Professor Jacques Reisse for very helpful discussions.

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