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**Optically Active Coordination Compounds. Part 50.¹
4-Fold Symmetry Axes in Optically Active Complex Ions from
Natural Nicotine**

R. D. Gillard and J. D. Pedrosa de Jesus

*School of Chemistry and Applied Chemistry, University of Wales College of Cardiff,
Cardiff CF1 1XL.*

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The synthesis, characterization and circular dichroism under varied conditions (notably pH) of *trans*-dichloro-tetrakis-(*S*)-(—)-nicotiniumrhodium(III) salts are described, to illustrate the interplay of chirality of the metal ion (D_4) and at carbon centres (C_1).

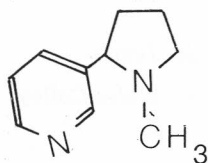
INTRODUCTION

In connection with the synthesis of carbonaceous molecules with only three-fold axial symmetry (the C_3 axis being common enough, among *tris*-chelated complex ions of the transition metals), the interesting remark was made that »organic chemists march to the beat of a different drummer«.

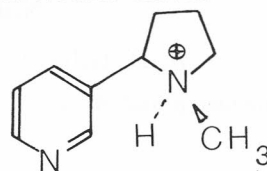
Indeed, one of the more fascinating fields of chiral stereochemistry has been the attempt to bring these differing beats into a common rhythm by studies of metal ions in geometries lacking mirror symmetry (particularly D_3 , C_3 , C_2 , C_1) with the ligands, normally chelating, containing an »asymmetric carbon atom« or other organic source of chirality. This contribution describes

the application of the stereochemical method to a novel point group, D_4 , in such a compound. The four-fold axis is formed by the *trans*-dichlororhodium(III) moiety, Cl—Rh—Cl, with perpendicular to it, the chiral element formed by the propeller shape of 4*S*-(—)-nicotine molecules bound *via* their pyridine nitrogens. These are protonated at the pyrrolic nitrogen atoms for synthetic convenience. The simplest possible D_4 species from a unidentate asymmetric donor such as *S*-nicotine would contain a planar array of the four nicotine ligands only, as in $[\text{Pd}\{(S)\text{-nicotine}\}_4]^{2+}$ ions. We report crystallographic work on the actual conformation of such ions elsewhere.² The present compound was mentioned briefly at a conference.³

(*S*)-(—)-nicotine (1), the alkaloid, occurs in tobacco leaves.

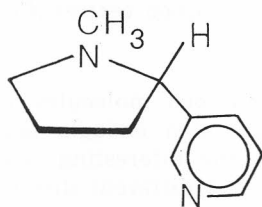


(1)

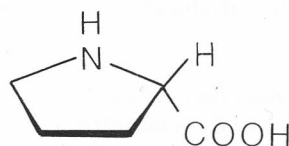


(2)

[abbreviated nicH⁺
in this paper]



(3)



(4)

The (*S*)-configuration (3) has been assigned with reference to both (*S*)-proline⁴ (4) and (*S*)-serine.⁵

The conformation in solution has been studied by NMR⁶⁻¹⁰ and dipole moment measurements.⁶ A quantum mechanical treatment of the conformation and electronic properties has also been reported.¹¹

Its chiral properties have received great attention for a hundred years. Lowry reports¹² early investigations on the optical activity of the base and its salts. Several ostensibly peculiar observations call for further investigation, for example, »the high laevorotatory power of the base and the reversal of sign in its salts and some other derivatives« and the variation in rotation of nicotine in different solvents: typically, $[\alpha]_D^{20}$ ranges from -19 in $\text{C}_2\text{H}_4\text{Br}_2$ to $+30$ in HCONH_2 . The statement¹² that the isotropic absorption band at 265 nm »is weakened nearly ten-fold when the base is dissolved in water, instead of in cyclo-hexane« is not correct. »Derivatives of (*S*)-(—)-nicotine which are *N'*-quaternized (*N'* is the pyrrolidine and *N* is the pyridine nitrogen) show great enhancement of the maximum occurring at around 260 nm in acid solution. The analogous *N*-quaternized isomers show neither enhancement or shift of the maximum when studied under the same conditions. The same situation is obtained with *N,N'*-bis-quaternized (*S*)-(—)-nicotinium salts.«¹³

The influence of protonic and Lewis acids on circular dichroism and optical rotatory dispersion of (S)-(—)-nicotine has also been studied.^{14,15}

Nevertheless, coordination of nicotine as a substituted pyridine is an unexplored aspect of its chemistry. The coordination chemistry of heterocycles (pyridine, bipyridyl, phenanthroline*) is of continuing interest. Some organometallic adducts of nicotine with the actinides are known^{16,17} and compounds with Fe(II) and Cr(III) have also been reported.^{18,19}

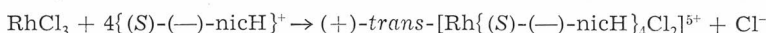
The preparation and characterisation of salts of the first complex of S-(—)-nicotine with Rh(III), (+)-*trans*-[Rh{(S)-(—)-nicH}₄Cl₂]⁵⁺ is reported here. The circular dichroism of the compound under different pH conditions is discussed, with particular emphasis on the relation to the stereochemistry of the complex.

Like other complex salts of pyridine (R-py), *trans*-[Rh{R-py}₄X₂]Y (X = Cl⁻ or Br⁻; Y = any anion), the present salts inhibit the growth of bacteria, but this and other interesting properties are described elsewhere.

RESULTS AND DISCUSSION

(+)-*trans*-Dichlorotetrakis-{(S)-(—)-1-hydronicotinium}-rhodium(III) Salts

Complexes of Rh(III) with (S)-(—)-nicotine may be prepared by a catalytic method similar to that used²⁰ to synthesise *trans*-[Rh(py)₄Cl₂]⁺ salts. An aqueous solution of the ligand hydrochloride is added to hot aqueous RhCl₃, the reaction being catalysed by the addition of a few drops of ethanol. The ligand, in these circumstances, is protonated¹⁴ at the pyrrolidine nitrogen: the reaction may therefore be written:



Yellow solids could be isolated with ClO₄⁻, PF₆⁻ and [B(C₆H₅)₄]⁻ as counterions. The chloride salt gave only yellow oils. Table I contains analytical

TABLE I
Analytical results for (+)-*trans*-[Rh{(S)-(—)-nicH}₄Cl₂]X₅ · nH₂O

Compound		C	H	N	Cl	P	F	Λ ₀ ^a
<i>trans</i> -[Rh(nicH) ₄ Cl ₂](ClO ₄) ₅ · 3H ₂ O	calc	34.85	4.79	8.13	18.04			62
	found	35.04	4.76	8.13	17.42			
<i>trans</i> -[Rh(nicH) ₄ Cl ₂](PF ₆) ₅ · 3H ₂ O	calc	29.9	4.4	7.0	4.4	9.4	35.5	
	found	30.5	4.1	7.3	4.8	9.7	35.1	
<i>trans</i> -[Rh(nicH) ₄ Cl ₂](BΦ ₄) ₅	calc	79.3	6.6	4.6				
	found	79.3	6.8	5.4				
<i>trans</i> -[Rhpy ₄ Cl ₂]Cl · 5H ₂ O ^b	calc	38.99	4.87	9.10				
	found	38.91	4.89	9.13				
<i>trans</i> -[Rh(γ-pic) ₄ Cl ₂](ClO ₄) ^b								33

^a From (linear) plots of equivalent conductance *vs* [complex]^{1/2} in H₃CNO₂ at 288 K; values for the nicotine complex were calculated supposing it to be a penta-positive ion; the linear plots had a negative slope for the nicotine species, because of ion-pairing, and a slightly positive slope for the γ-picoline analogue.

^b Method of reference 20.

^c γ-pic denotes 4-methyl pyridine.

* Blau, the discoverer of metal chelation by phenanthroline, was also active in work on nicotine.

TABLE II
 Electronic and circular dichroism spectra of $\text{trans-[RhL}_4\text{Cl}_2]^+$
 $L = \text{nicH, pyridine (py) or ethylenediamine (en)}$

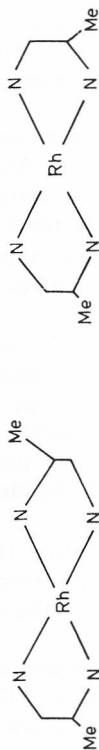
Compound	Electronic absorption		λ (nm)	ν (kK ^a) $10^{-1} \epsilon$ (mol ⁻¹ dm ²)	ν (kK ^a) $10^{-1} (\epsilon_L - \epsilon_R)$ (mol ⁻¹ dm ²)	Circular dichroism	
	λ (nm)	ν (kK ^a) $10^{-1} \epsilon$ (mol ⁻¹ dm ²)					
$(+)$ - <i>trans</i> -[Rh{(S)-(-)-niH} ₄ Cl ₂] · · (PF ₆) ₃ · 3H ₂ O	407	24.57	407	97 ^b	24.57	+ 1.12 ^b	
	272sh	36.76	300	12080	33.33	— 1.63 ^c	
	266	37.59	278	17995	35.97	+ 1.17	
	260	38.46	269sh	18770	37.17	+ 4.17	
	230	43.38	262sh	39075	38.17	+ 10.43	
			257		38.91	+ 12.38	
			228		43.86	+ 24.19	
	(S)-(-)-nicotine	265sh	37.74	268	2609	37.31	— 2.27
		260	38.46	262	3457	38.17	— 2.59
		256sh	39.06	256	3131	39.06	— 1.50
250sh		40.00	250sh	2435	40.00	— 0.24	
			245sh		40.82	+ 0.48	
210sh		37.62	236	5022	42.37	+ 0.87	
205sh		48.78	—	7030	—	—	
198		50.50	—	7850	—	—	
<i>trans</i> -[Rhp ₄ Cl ₂]Cl · 5H ₂ O	410	24.39	—	78	—	—	

^a 1 kK (kilokayser) = 10^3 cm^{-1} ; these wave numbers are simply the reciprocals of the measured wavelengths.

^b These SI units have been multiplied by 0.1 to give the more familiar »molar extinction coefficients« and »molar circular dichroisms«.

^c This negative band is discussed in the text.

^d See J. H. Dunlop and R. D. Gillard, *Mol. Phys.* **7** (1964) 493: these CD results on *trans*-[Rh(1-pn)₂Cl₂]⁺ referred to a synthetic sample, of unknown isomeric nature in the following sense. Whereas *trans*-[M(A)₄X₂]⁺ ions, with A a unidentate amine (possibly optically active) may possess a genuine C₄ axis parallel with the X—M—X line, this is not so for *trans*-[M(AA)₂X₂]⁺, AA being a diamine like en or (+)bn, with two equivalent nitrogen atoms. It may be even less so, *sensu stricto*, for the case where AA is a truly asymmetric 1,2-diamine like, 1,2-diaminopropane, where, even for the optically pure case, *trans*-[M(R-pn)₂X₂]⁺, there are two isomers shown, viewed along the X—M—X line. (This pair of isomers is akin to the fac:mer pair for [Rh(R-pn)₃]³⁺ whose existence has given rise to difficulties).



The assignments of transitions based on the comparison of AA = en with AA = 1-pn is justified on the grounds that the tetragonal perturbation of the octahedral parent states is very much greater than any perturbation or loss of tetragonal E-degeneracy arising from the distribution of the peripheral substituents on asymmetric carbon atoms.

This minor isomerism seems not yet deliberately to have been studied for asymmetric diamines (it is, of course, identical in terms of symmetry to the classical problem of the *cis-trans* isomerism in [Cu(l-aminoacacate)₂]).

results. Assignment of the *trans*-dichloro-configuration relies on the electronic spectrum (in the d—d region) akin to those of compounds *trans*-[RhL₄Cl₂]⁺, where L = pyridine, amine, 1/2 en (Table II). Such complexes where L = pyridine or substituted pyridine are not indeed yet known in the isomeric *cis*-configuration, although well-established cations containing the moiety *cis*-tetrakispyridine (octahedral) metal ion do exist, in [M(py)₆]²⁺ salts, and in the oxalatotetrakispyridineruthenium(II) species, ruthenium(II) being, of course, isoelectronic with rhodium(III).

Electronic and Circular Dichroism Spectra

The electronic spectrum of (+)-*trans*-[Rh{(S)-(—)-nicH}₄Cl₂]⁵⁺ shows a first absorption band centered at 407 nm ($\epsilon = 970 \text{ mol}^{-1} \text{ dm}^2$; note the units, which are ten times smaller than those of classical »molar extinction coefficients«). This is the region in which compounds of the type *trans*-[RhL₄Cl₂]⁺, where L = pyridine or 1/2 en, have their first absorption band, assigned — for the centric ions with *D*_{4h} symmetry — to ¹E_g ← ¹A_g (Table II). In the ultra-violet region, the spectrum of the complex shows a structured band centered around 265 nm. Similar absorptions are observed for free nicotine. The spectrum of nicotine in this region is due mainly to transitions within the pyridine ring. These are not much different from pyridine itself ($\pi^* \leftarrow n$: $\doteq 275 \text{ nm}$; $\pi^* \leftarrow \pi$: $\doteq 250 \text{ nm}$).²¹ In the complex, there are no $\pi^* \leftarrow n$ transitions. Absorptions around 265 nm are due to $\pi^* \leftarrow \pi$ and metal → ligand transitions.

Note that the complex ion, being optically active, must be non-centric: descriptions of orbitals are therefore inaccurate because there are — *sensu strictu* — no gerade or ungerade states. However, we use the d-nomenclature because the perturbation of symmetry at the metal ion represented by the difference in point group between centric *D*_{4h} and non-centric *D*₄ is small as shown by the change in the degree of Laporte-forbidden character in Table II: $\epsilon(D_4) = 970$; cf. $\epsilon(D_{4h}) = 780$ or 820 .

Essentially then, to a very good approximation, the d—d transitions of a spin-paired 4d⁶ ion like the present rhodium(III) correspond to excitation from non-bonding d-levels to anti-bonding d-levels rather akin to $\pi^* \leftarrow n$ bands in other familiar chiral molecules.

The circular dichroism of the complex in aqueous solution at room temperature shows a positive Cotton effect centred at 407 nm with a *g* factor of 1.16×10^{-2} corresponding to a magnetic-dipole-allowed transition. This absorption, for *D*_{4h} symmetry, involves essentially the transference of an electron from d_{xz} and d_{yz} orbitals to the d_{z²} orbital, so there are translatory (μ_c) and rotatory (μ_m) movements, equivalent in conjunction to a helical path, of the electron in the transition. Since the solution shows $\epsilon_L - \epsilon_R > 0$ for this transition, the excited electron must be constrained to move in a righthanded helical path. This chirality around the dichloro-metal »spindle« is the consequence of a four-bladed propeller comprising the pyridine rings of the (S)-(—)-nicotine ligands. Molecular models suggest that such an arrangement of the ligands (the pyridine plane making an angle around 45° with the Rh^{III}N₄ plane) is sterically favoured. While detailed description of configurations adopted by four planar ligands arranged on a spindle is not necessary here, there are some relevant crystallographic findings in *trans*-dihalo-octahedral

systems like the present ones. The crystal and molecular structure²² of *trans*-[Rhpy₄Br₂]Br · 6H₂O was said to show that the four pyridine ligands form a propeller with a dihedral angle of some 45°. Although that original report has not been amplified, the cation in the low temperature dimorph of *trans*-[Irpy₄Br₂]Br · 5H₂O indeed had²³ just such a conformation. Subsequently, the dibromo-rhodium bromide was again shown²⁴ to be isostructural with the iridium species.

The strong circular dichroism bands in the region 250—270 nm are less simple to analyse. They probably derive from transitions localized on ligands. The $\pi^* \leftarrow \pi$ transitions expected in this region are polarized in the plane of the pyridine residue, along a direction nearly perpendicular to its N—C(4) axis, and may possibly be treated using the exciton model. If this is so, the observed optical activity of the multi-chromophoric system is the result of the coupling by Coulombic interactions of the electronic transition moments of the individual groups in the molecule. The positive Cotton effect then implies that the resultant transition in this region takes place in a right-hand helical path. Qualitatively, this is the expected result of the addition of the four linear vectors representing the $\pi^* \leftarrow \pi$ transition in each pyridine ring. The configuration deduced would agree with that more confidently derived above from the positive CD at 407 nm.

The spectroscopic results of Table II support the assignment of the absorption at 250—280 nm as a ligand-centred allowed transition with vibrational components ($\Delta\nu$ is around 800—1000 cm⁻¹, reminiscent of the similar observations²⁵ in chiral benzenes). Further, there is little change in the vibrational manifold from parent free nicotine to complex.

The one unassigned band in circular dichroism (there is no clear counterpart in isotropic absorption) is at 300 nm; its negative sign shows it to be distinct from the ligand-centred transition at 260 nm. It arises, almost certainly, from another of the d—d transitions within the d⁶ spin-paired manifold. For such complex ions of D_{4h} symmetry, the lowest energy spin allowed transition of O_h parentage ${}^1T_{1g} \leftarrow {}^1A_{1g}$ splits into ${}^1E_g + {}^1A_g \leftarrow {}^1A_{1g}$. The 1E_g component lies at lower energy, and corresponds to the transition already discussed at ~407 nm. The other component corresponds to a transition within the planar four nitrogen Rh^{III}N₄ chromophore, and is centred around 300 nm, like ${}^1T_{1g} \leftarrow {}^1A_{1g}$ of many [Rh^{III}N₆] chromophores, [Rh(NH₃)₆]³⁺ etc. The present value jibes well with other *trans*-RhN₄Cl₂⁺ species like [Rh(en)₂Cl₂]⁺ (Table II) and *trans*-[Rh(pn)₂Cl₂]⁺ (of unknown geometric structure, where pn = (+)-1,2-diamino-propane), where the circular dichroism engendered by the chiral field of the asymmetric carbon atoms in the chelating ligands includes the two bands shown in Table II, at 410 nm, and at 298 nm. The second d—d component in *trans*-[Rh(R-py)₄Cl₂]⁺ has not previously been located, showing yet again how useful circular dichroism can be in revealing weak magnetic-dipole allowed bands in complex molecules.

Addition of OH⁻ to (+)-*trans*-[Rh{(S)-(-)-nicH}₄Cl₂]⁵⁺ Ions

When a solution of (+)-*trans*-[Rh{(S)-(-)-nicH}₄Cl₂]⁵⁺ salt of a strong acid is titrated with sodium hydroxide, one clear inflection point (pH = 9.5) is observed in the titration curve, which corresponds to the addition of 3.7 moles

of OH^- per mole of complex. The acidity constant, $\text{p}K_a$, determined from this titration is 8.5 at 291 K. Reported $\text{p}K_a$ values for the pyrrolidine proton of protonated nicotine are 8.03 at 298 K and 7.92 at 288 K. The end point of our titration corresponds to the titration of four protons in the complex, but it is (not surprisingly) not possible to distinguish individual acidity constants for the four initially equivalent protons on the four spatially well-separated pyrrolidine residues of the nicotine ligands.

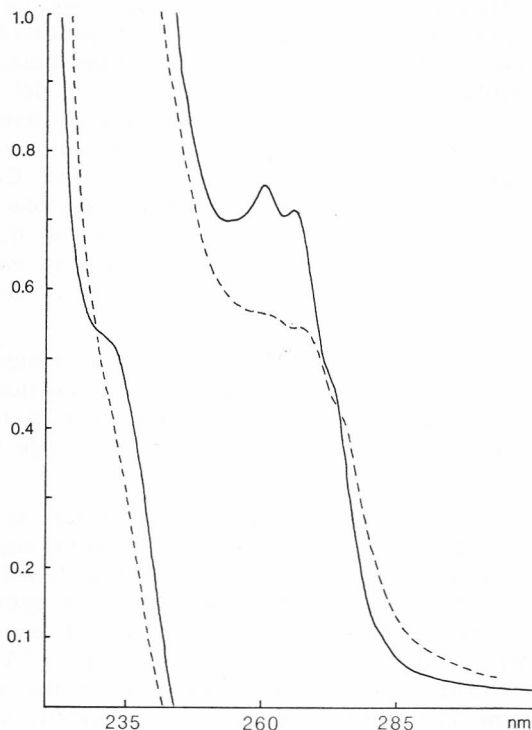


Figure 1. Electronic spectra of dilute (+)-*trans*- $[\text{Rh}\{(\text{S})\text{-(–)}\text{-NicH}\}_4\text{Cl}_2]^+$ (—) in H_2O and (---) in 10^{-2} M KOH: there is a vertical scale (absorbance) discontinuity at ca 244 nm. The longer wavelength (> 244 nm) data have been multiplied by 10.

The addition of hydroxide ion to aqueous solutions of the complex has a dramatic effect on its electronic (Figure 1) and CD spectra (Figure 2). During this titration, up to pH about 10.5, the absorption in the visible region does not change significantly and nor does the CD at 407 nm. This constancy for the d–d region, the indication of chirality along the Cl–Rh–Cl axis, shows that overall propellor handedness is unchanged. However, the positive band centred around 260 nm in the CD spectrum loses much intensity. Meanwhile, a new negative band grows centred at about 275 nm. As Figure 3 shows the intensities of both bands vary linearly with $[\text{OH}^-]$ and then remain constant until pH about 10.5.

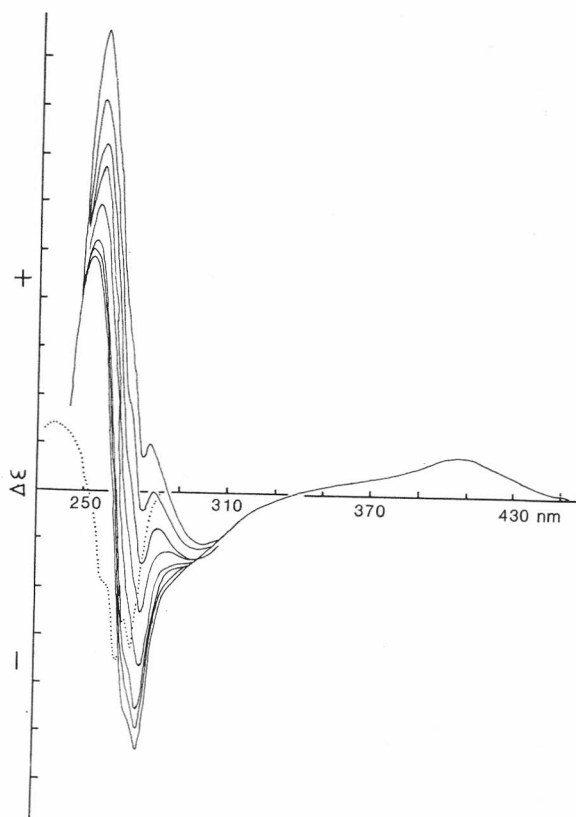


Figure 2. Changes in the CD spectrum of *trans*-[Rh{(S)-(-)-nicH}₄Cl₂]⁵⁺ upon addition of OH⁻. For details see text.

These final CD spectra (albeit shifted in energy) are now very similar to the CD spectrum of parent (S)-(-)nicotine, implying a change of conformation in the organic ligand but *not* around the metal ion.

Upon further addition of OH⁻ to the now »neutral« nicotine complex, a light yellow solid forms, which is stoichiometrically the hydrated »hydroxide« of *trans*-[Rh(nic)₄Cl₂]⁺. However, just as for quaternized derivatives of *N*-heterocycles, there is an ambiguity between the ionic hydroxide and the tautomeric ψ -base. We formulate our light yellow precipitate at high pH as the ψ base, CB, of Scheme 1. CB was collected and dried: the CD spectra of its solutions in acetone and in nitromethane show a *negative* Cotton effect, at around 410—415 nm. However, the CD of the filtrate gives a positive Cotton effect in the same region. The shape of this CD spectrum (negative at *ca* 470 nm: positive at *ca* 370 nm) appears to result from the addition of a positive band centred around 407 nm to the negative one of CB around 412 nm. That is, some sort of equilibrium is established for species in the filtrate. These species must be responsible for the different Cotton effects in turn, and the species giving a negative Cotton effect precipitates at high pH to give the yellow solid CB. The CD spectrum of the yellow solid CB in nitromethane changes completely on addition of two drops of concentrated nitric

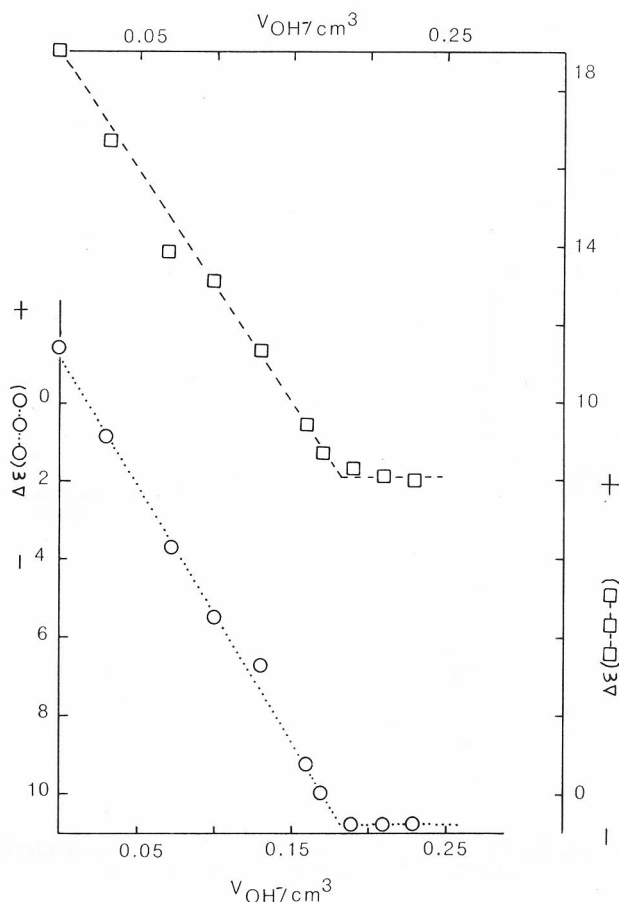
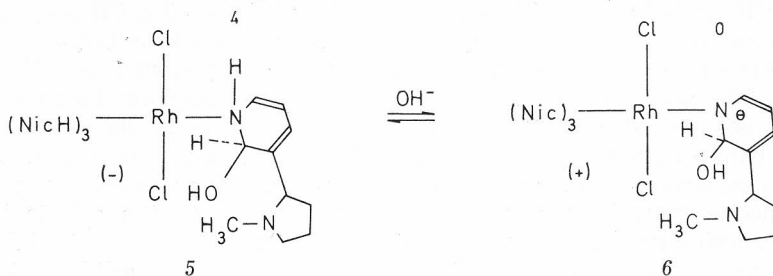


Figure 3. Change in the intensity of the CD bands of $trans\text{-}[\text{Rh}\{(S)\text{-}(-)\text{-nicH}\}_4\text{Cl}_2]^{5+}$ at 275 nm (○ ··· ○) and 257 nm (□ --- □) upon addition of OH^- .

acid. The new spectrum shows a positive Cotton effect centred around 410 nm about 50 times more intense than that of the alkaline product, and much more intense than that of the original $trans\text{-}[\text{Rh}\{(S)\text{-}(-)\text{-nicH}\}_4\text{Cl}_2]^{5+}$ ion.

The stereoselective addition of base to the nicotine complex results in the formation of a new species CB with new elements of chirality. The



Scheme 1: Proposed chirally distinct species in titration with hydroxide of the penta-positive ion: (+)- $trans\text{-}[\text{Rh}\{(S)\text{-}(-)\text{-nicH}\}_4\text{Cl}_2]^{5+}$.

reaction is reversible, the original electronic and CD ($\lambda = 407$ nm; positive) spectra being regenerated upon slow addition of the acid to the alkaline product in water. The reactions are summarized in Scheme 1.

Reactions of coordinated heterocycles with nucleophiles have been studied²⁶ in these laboratories. The mechanism proposed for such reactions involves the attack of the ligand in a position *ortho* to the metal bonded nitrogen, giving species like 5 and 6. In particular, addition of OH⁻ to *trans*-[Rh(py)₄Cl₂]⁺, leads to the precipitation of a yellow solid, soluble in acetone. Although the nature of this product is not yet clear, the nicotine results seem to support the formation of covalent hydrated species (like 5) and/or the corresponding pseudobase (like 6).

Reversible reactions take place upon addition of base to the Rh(III) nicotine complex. The mechanism proposed (Scheme 1) is given as a first approximation to rationalize the observations. The power of the stereochemical method in evaluating chemical equilibria and other reactions is particularly clear in this type of complex where there is such subtle interplay of organic asymmetry and the dissymmetry of coordinated metal ions.

EXPERIMENTAL

trans-[Rh{(S)-(-)-nicH}₄Cl₂](ClO₄)₅·3H₂O

A solution of RhCl₃·3H₂O (0.275 g ~ 1 mmol) in 5 ml water was heated on a steam bath. A solution containing 2 cm³ (~11 mmol) of (S)-(-)-nicotine, 2 cm³ of water and 1 cm³ of concentrated HCl (final pH around 6) was added to the hot solution of RhCl₃. This was then heated on a free flame and a few drops of ethanol were added: the initial red colour rapidly became yellow. Heating continued for 5 minutes. NaClO₄ (0.9 g ~ 6 mmol) was then added to the hot solution which was allowed to cool, first on the bench and afterwards in ice. A yellow solid forms: this was collected by filtration, washed with ice-cold water, ethanol, then ether, and air dried (m = 0.4 g). Addition of another 1.5 g of NaClO₄ to the filtrate gave more product. This was treated as above to yield another 0.5 g. Total yield 62%. The analytical sample was recrystallized from H₂O.

trans-[Rh{(S)-(-)-nicH}₄Cl₂](PF₆)₅·3H₂O

The reaction of RhCl₃·3H₂O with S-(-)-nicotine was carried out as above, and NaPF₆ (0.33 g ~ 2 mmol) was added to the hot final yellow solution. A yellow solid forms on cooling to room temperature; this was collected, recrystallized from hot water, washed with ice-cold water, ethanol, then ether, and dried *in vacuo*, over silica gel (m = 415 mg). To the filtrate, more NaPF₆ (1.00 g ~ 6 mmol) was added. On cooling to room temperature, a yellow «oil» comes down, leaving a clear solution. This is separated by decantation. The oily residue is then redissolved in hot water and crystallized by cooling to room temperature. Two recrystallizations were carried out. The final product was washed with ice-cold water, ethanol then ether, and dried *in vacuo* over silica gel (m = 330 mg). This sample was used for analysis. On concentrating the filtrate on a water bath and adding still more NaPF₆, further amounts of complex (~400 mg) can be obtained.

trans[Rh{(S)-(-)-nicH}₄Cl₂](BΦ₄)₅

This compound was obtained by adding sodium tetraphenylborate to part of a solution resulting from the preparative step for the perchlorate: a yellowish solid formed immediately, insoluble in water. It was washed with water, dried *in vacuo* over silica gel, and recrystallized by slow evaporation of a solution in acetone. The solid, initially yellow, turns light brown with time.

In attempts to precipitate the complex with NaBF₄, a green solution was obtained, which, apart from the expected 407 nm band shows another absorption

centred at around 650 nm, This probably arises from formation of a μ -superoxo-dirhodium(III,III) species. Such bands often appear in alkaline solutions of N-heterocyclic compounds of rhodium(III) in the presence of di-oxygen of air.

Reaction with Oxalate

(+)*trans*-[Rh{(S)-(—)-nicH₄Cl₂}(ClO₄)₅·3H₂O (70 mg) in water (20 cm³), pH = 6–7: (λ = 407 nm) as treated with sodium oxalate (40 mg) and the pH adjusted to 10 (dilute NaOH). The solution was set to reflux for 10 minutes and filtered. The band at 407 nm disappears and a new shoulder is observed around 350 nm, from [Rh(nic)₃Cl(C₂O₄)].

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SAŽETAK**Četverostruka os smeirije u optički aktivnom kompleksnom ionu prirodnog nikotina**

R. D. Gillard i J. D. Petrosa de Jesus

Opisana je sinteza, karakterizacija i cirkularni dikroizam u različitim uvjetima (posebno pH) *trans*-dikloro-tetrakis-(S)(-)-nikotinijeve Rh(III)-soli. Ilustriran je međusobni odnos kiralnosti metalnog iona (D_4) i kiralnog centra na ugljikovu atomu (C_1).