Tetrahedron: Asymmetry Vol. 3, No. 2, pp. 307-312, 1992
Printed in Great Britain

0957-4166/92 $3.00+.00
Pergamon Press plc

SYNTHESIS AND CHARACTERIZATION OF Ru(III) CHIRAL SCHIFF BASE COMPLEXES DERIVED FROM SUBSTITUTED ALDEHYDES AND L-HISTIDINE

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(*Received* 2 *January* 1992)

Abstract: Ruthenium(III) Chiral Schiff base complexes derived from L-histidine with pyridine 2-carboxyaldehyde, 5-methoxy and 5-chloro salicylaldehyde have been synthesized. The complexes were characterised by elemental analysis, IR, UV-visible spectroscopy, conductance measurement, magnetic susceptibility, electrochemical studies, optical rotation and circular dichroism spectra. The conformational aspects regarding the asymmetric arrangement of substituted Schiff base ligands around ruthenium(III) ion have been discussed. All the complexes show an irreversible redox potential in the range -0.36 to -0.40 volts corresponds to Ru(III)/Ru(II) redox couple. In the case of the 5-substituted salicylaldehyde this show linear dependence on Hammet parameter σ_p.

Introduction

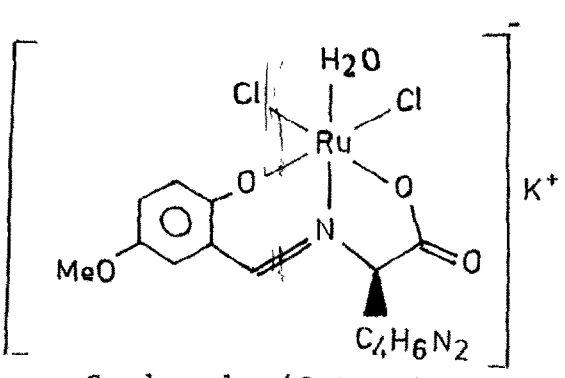
Aminoacids and their fluoroanalogues have received much attention as antifungal, antitumor and chemotherapeutic agents in recent years[1-4]. The fundamental requirement in the design of these compounds is to obtain an aminoacid material with high optical purity. A variety of organoruthenium(II) complexes of aminoacids such as glycine, D,L-alanine, L-valine and L-phenylalanine with norbornadiene and 1,5 cyclooctadiene have also been reported[5].

In continuation of our previous work[6] we present in this communication the synthesis and structural characterization of ruthenium(III) Chiral Schiff base complexes derived from substituted aldehydes viz. pyridine 2-carboxyaldehyde, 5-methoxysalicylaldehyde and 5-chlorosalicylaldehyde with L-histidine. The steric and conformational aspect around ruthenium(III) ion are reported.

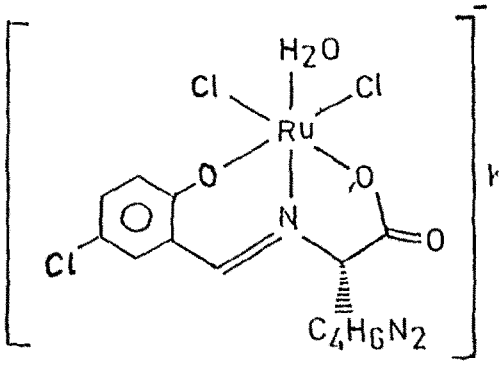
Results and Discussion

All chiral Schiff bases were synthesized by reported procedure[7]. The ligands derived from 5-chloro and 5-methoxy salicylaldehyde are yellow in colour while that of pyridine 2-carboxyaldehyde is brown. These complexes are highly air sensitive. The ligands have been characterized by physicochemical methods[7,8].

The stoichiometric composition of the complexes 1-3 is consistant with the elemental analysis. Millimolar solution of the complexes 1 and 2 in methanol correspond to a 1:1 electrolyte (85-90 Ohm^{-1} cm^2 mol^{-1}) while the complex 3 is a non-electrolytic in the solvent (5 Ohm^{-1} cm^2 mol^{-1}). The magnetic suspectibility of the complexes lie in the range 1.99 to 2.08 B.M. showing the paramagnetic nature of the complexes.



Complex - 1 (S form)



Complex - 2 (R form)

In the IR spectra of the ligands and the complexes a band near 1635-1600 cm^{-1} is due to azomethine group which overlaps with the asy-COO streiching modes and the C = C/C=N ring streiching bands. This band undergoes a modest decrease on complexation to the metal ion[9]. The sym(-COO) stretching vibration lie at 1415 cm^{-1} while the ring streiching viration lie at 1354, 1130 and 1475 cm^{-1} in all the

Table 1: Optical rotation, Electronic Absorption and C.D. spectral data for Ru(III) Chiral Schiff base complexes

	Complexes	Abs. configuration	$[\alpha]_D^{25}$ deg.$cm^{-2}g^{-1}$	λ_{max} (εM^{-1} cm^{-1})	ν kK ($\Delta\varepsilon$)
1.	5-MeO Sal L-hisdichloroaquo-ruthenate(III)	S	+124.6°	550^{sh}(400), 373(1281), 270(2322)	30.3(-1.33), 25.0(+0.78), 21.5(-0.12), 18.0(+0.4)
2.	5-Cl Sal L-hisdichloroaquo-ruthenate(III)	R	-90°	601(372), 320(1596)	31.2(-1.7), 25.3(+0.89), 19.0(+0.32)
3.	Pic L-hisdichloroaquo-ruthenate(III)	R	-137.2°	510(748), 366(1328), 342(1500)	31.2(-1.2), 23.5(+0.29), 19.8(+0.31), 18.8(+0.29)

complexes. In complexes 1, 2 and 3 a broad band at 3400 cm^{-1} along with two deformation bands at 1100 and 1170 cm^{-1} have been assigned to ν(O-H) and δ(O-H) modes, respectively. These results are in consonance with those reported earlier[10]. In the far IR region ν(Ru - Cl) and ν(Ru - N) lie near 330 to 345 cm^{-1}.

The electronic spectra of complexes 1 and 2 recorded in methanol and that of complex 3 in acetonitrile show high intensity charge transfer band near 270 nm (ε = 2322) while the LMCT band lie near 320 (ε = 1596) to 373 (ε = 1281) nm. The position of LMCT bands also depend on the substituents attached on the ring moiety of the Schiff base[11]. The energy of the band decrease in the order 5-Cl Salhis 2 > 5 CH_3O Salhis 1 > Salhis[6] ~pic his 3. The d-d bands lie near 510 (ε = 748) and 601 (ε = 372) nm.

The C.D. spectral data is summarised in Table I. The C.D. spectra of 5-MeO Salhis (Fig.Ia) is quite similar to that of 5-Cl Salhis (Fig.Ib). They show

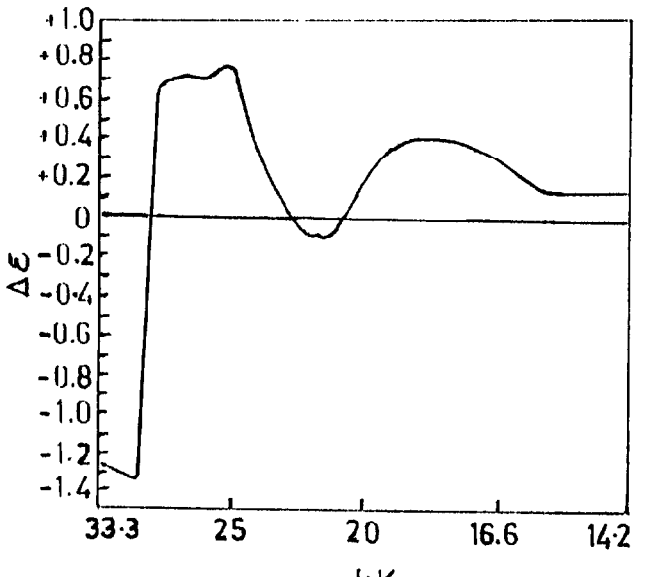


Fig. Ia C.D. spectrum of 5 MeO Sal L-his-dichloroaquo ruthenate(III) complex in methanol

a slight difference in the C.D. intensity as compared to the unsubstituted complex which is comparable to the C.D. effect due to the presence of withdrawing (5-Chloro) and donating (5-MeO) group in the close vicinity of asymmetric C atom containing L-histidine. The structure of the complexes reveal that the 5-MeO Salhis complex has a non-bonded interaction between the histidine molecule and methoxy group

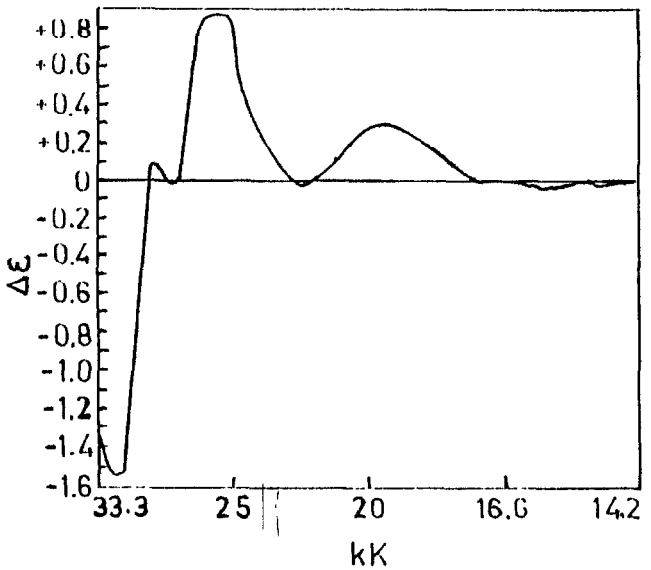


Fig. Ib C.D. spectrum of 5Cl Sal L-hisdichloro-aquoruthenate(III) complex in methanol

while 5-chloro Salhis does not have such a steric interaction. This suggests that the strain for conformation of the ligands affect the C.D. intensity without the C.D. patterns[12]. Due to the steric interaction between the methoxy and the histidine molecule complex 1 acquires the SS configuration in methanol which is also evidenced by its optical rotation $[\alpha]_D^{25}$ = +124.6

While in the complexes 2 and 3 the ligand is stereo specifically coordinated to ruthenium moiety so that the gauche chelate ring is located in λ conformation with small preferences δ form. Similar relationships among C.D. spectra were also reported earlier[6,12,13]. Thus in all the complexes the steric interactions between substituents at the azomethine group and those on the chelate ring provide the driving force for both the preferred conformation and configuration.

In the ligand field region the C.D. bands with positive Cotton effect at 18.0 to 19.8 kK have been assigned to both the d-d bands and spin forbidden ligand bands. This band undergoes blue shift with an increase in the donor strength of the group attached to the schiff base moiety[12]. The charge transfer band lie at 21.5 to 25 kK due to $d \rightarrow \pi^*$ transition of the azomethine group. In the higher energy region the ligand $\pi \rightarrow \pi^*$ azomethine transition band lie at 30.30 to 31.25 kK. The shift of both the charge transfer and ligand transition with azomethine substituents is consistent with the inductive effect of the donating or withdrawing group on the ligand levels[14].

The cyclic voltammogram D.C. polarogram and differential pulse polarogram was recorded in methanol water mixture with 0.1N $NaClO_4$ as supporting electrolyte vs Ag/AgCl. The complexes show irreversible behaviour and Ru(III)/Ru(II) reduction potential lie in the range -0.36 to -0.40 volts versus Ag/AgCl for all the complexes (Table II). The $E_{\frac{1}{2}}$ values were plotted as a function of the Hammet σ_p parameter

for unsubstituted[6] and 5 substituted salicylaldehyde. The linear relationship indicate that the electronic effect of a substituent is transmitted through ligand to the metal in the complexes[11].

Table 2: Electrochemical data of 5 substituted Chiral Schiff base complexes. (vs. Ag/AgCl) at 25°C

Complex	Substituent parameter σ_p	$E_{\frac{1}{2}}$
5MeO Sal-his	-0.27	-0.36
5Cl Sal-his	+0.23	-0.40
Pic-his	--	-0.34
Sal-his	0	-0.38

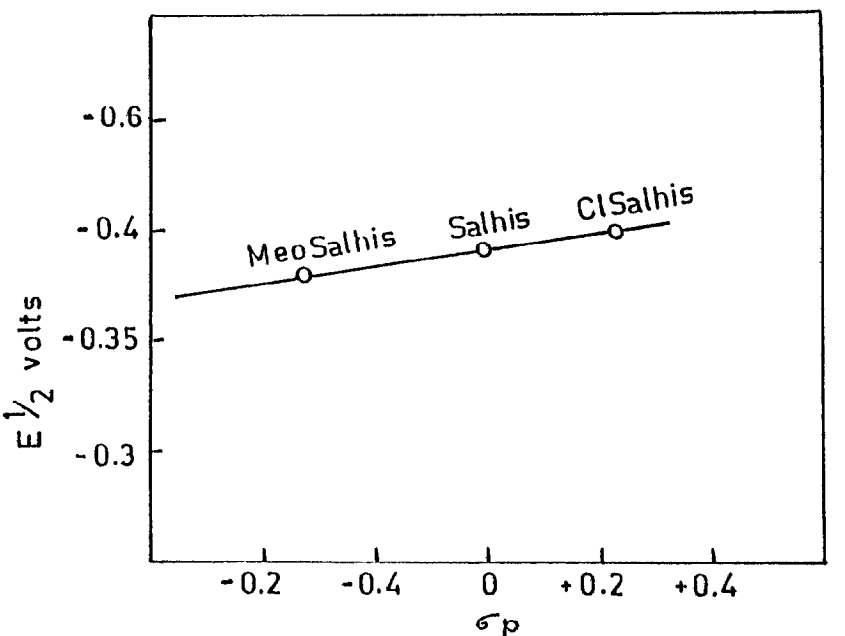


Fig.II Plot of the $E_{\frac{1}{2}}$ values vs the Hammett σ_p for 5 substituted Chiral Schiff base complexes

Experimental

$RuCl_3.3H_2O$ was from Johnson and Mathey. The compounds 5-chlorosalicylaldehyde, 5-methoxysalicylaldehyde, pyridine 2-carboxyaldehyde, L-histidine were synthesized by known procedure[6,7]. All the complexes were prepared under argon atmosphere. The progress of the reaction were checked by TLC from time to time.

Preparation of the complexes

To a hot methanolic solution (1.0 mmol) of the above Schiff bases were added (1.0 mmol) of $K_2[RuCl_5(H_2O)]$ in a 1:1 metal: ligand ratio. The reaction mixture was refluxed to 10-12 hrs in an argon atmosphere. The completion of the reaction was checked on TLC. After that the solution was filtered under an argon atmosphere. The filtrate was concentrated to about 10 ml and the complexes precipitated by diethylether. The complexes were recrystallized in the same solvent. They were dried in vacuo yield: 59%. Anal. Calc. for complex 1, C,32.26; H,2.68; N,9.20. Found: C,32.05; H,2.65; N,9.13. Complex 2, C,30.07; H,2.11; N,8.08. C,30.02; H,2.10; N,8.07. Complex 3, C,33.26; H,3.02; N,12.92. C,33.21; H,3.01; N,12.89.

Physical measurements

Micro analysis of the complexes were performed on a Carlo Erba Analyser Model 1106. Molar conductance was measured at room temperature on a Digisun electronic conductivity bridge. The IR spectra were recorded on Carl Zeiss Specord M-80 spectrophotometer in Nujol mull/KBr. Electronic spectra were recorded on a Shimadzu UV-visible recording spectrophotometer model 160. The magnetic moment measurements were made at 298°K by Gouy method using $Hg[Co(SCN)_4]$ as calibrant and experimental susceptibilities were corrected for diamagnetism. Cyclic voltammogram, d.c. Polarogram and differential pulse polarograms were recorded with a Princeton Applied Research (PAR) instrument. The optical rotation of the complexes in methanol and acetonitrile was measured by polarimeter DIP-360 Jasco Machine. The C.D. spectra were recorded in methanol by Jobin YVON-Paris.

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