Tetrahedron: Asymmetry Vol. 2, No. 10, pp. 1015-1020, 1991
Printed in Great Britain

0957-4166/91 $3.00+.00
Pergamon Press plc

SYNTHESIS AND CHARACTERIZATION OF Ru(III) CHIRAL SCHIFF BASE COMPLEXES DERIVED FROM SALICYLALDEHYDE AND L-AMINOACIDS

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(*Received* 1 *July* 1991)

Abstract: The synthesis and characterisation of several chiral ruthenium (III) Schiff base complexes of the type $K[(Ru(L)(Cl)_2(H_2O)]$ where L = Schiff base derived from L-aminoacids with salicylaldehyde are reported. The electronic absorption, optical rotation and circular dichroism spectra of the complexes in methanol are discussed.

Introduction

Transition metal complexes of aminoacids constitute model systems for the study of metalloproteins[1] including their molecular structure[2] as well as their electronic and magnetic properties.[3,4]

The chemistry of metal complexes with multidentate ligands with delocalized π-orbitals such as Schiff bases[5,6] or porphyrins[7] has recently gained much interest because of their use as models in biological systems especially those of respiratory pigments or the coenzymes of vitamin B_{12}. The complexes of $[RuCl_2(PPh_3)_3]$ with L-aminoacids like L-glycine, L-serine, L-hydroxyproline and L-allohydroxyproline show a square pyramidal geometry and are of potential utility as homogeneous catalysts.[5] The catalytic properties of oxovanadium(V) and oxovanadium(IV) complexes with quadridentate Schiff base ligands have also been reported.[6] The chiral phosphine complexes of ruthenium(II) have gained importance in asymmetric hydrogenation.[8]

In order to develop new chiral ruthenium(III) complexes we have synthesised Ru(III) chiral Schiff base complexes derived from L-aminoacids such as L-alanine (L-ala), L-phenylalanine (L-pheala), L-valine (L-val), L-serine (L-ser), L-aspartic acid (L-asp), L-methionine (L-meth), L-histidine (L-his), L-cystein (L-cys), L-tyrosine (L-tyr) and L-arginine (L-arg) with salicylaldehyde. The steric and conformational effects with various R groups attached to the aminoacid moiety in chiral Schiff base metal complexes are reported in this paper.

Results and Discussion

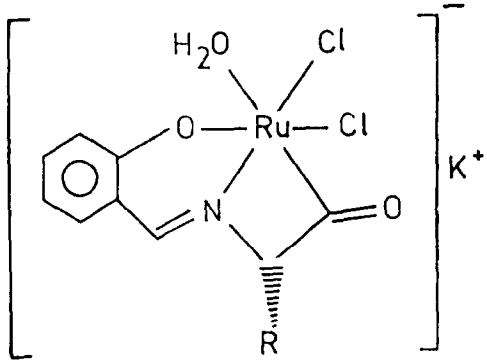
All optically active Schiff base ligands were synthesised by the reported procedure.[9] The ligands are all yellow in colour and are highly air sensitive. The complexes were synthesised under an argon atmosphere and characterised by elemental analysis, IR and ^1H NMR spectroscopic methods.[9,10]

Table I Analytical data, molar conductance, optical rotation and absolute configuration in Chiral Ru(III) Schiff base complexes

Complexes	Found (Calc) %C	%H	%N	Molar conductance Λ_M Ohm^{-1} cm^2 mol^{-1}	Abs. configuration	$[\alpha]_D$ deg. cm^{-2} g^{-1} (in MeOH)
1. Sal-L-Valdichloroaquoruthenate(III)	33.19 (33.26)	3.40 (3.46)	3.19 (3.23)	85	R	-214.8°
2. Sal-L-Argdichloroaquoruthenate(III)	33.00 (33.06)	3.12 (3.17)	8.82 (8.89)	90	R	-119.8°
3. Salt-L-Hisdichloroaquoruthenate(III)	33.22 (33.31)	2.50 (2.56)	8.91 (8.96)	85	R	- 62.2°
4. Sal-L-Aladichloroaquoruthenate(III)	28.53 (28.59)	2.59 (2.61)	3.30 (3.33)	100	R	-227.4°
5. Sal-L-Methdichloroaquoruthenate(III)	32.08 (32.12)	3.30 (3.34)	3.09 (3.12)	105	R	-202.4°
6. Sal-L-Aspdichloroaquoruthenate(III)	32.22 (32.28)	1.90 (1.95)	3.40 (3.42)	90	R	-119.8°
7. Sal-L-phealadichloroaquoruthenate(III)	38.29 (38.32)	2.95 (2.99)	2.73 (2.79)	95	R	-192.6°
8. Sal-L-cysdichloroaquoruthenate(III)	27.51 (27.54)	2.50 (2.52)	3.18 (3.21)	85	R	- 64.8°
9. Sal-L-Tyrdichloroaquoruthenate(III)	37.42 (37.49)	2.89 (2.92)	2.71 (2.73)	105	R	- 49.8°
10. Sal-L-Serdichloroaquoruthenate(III)	27.50 (27.54)	2.50 (2.52)	3.17 (3.22)	95	R	- 77.2°

Table II Electronic Absorption and C.D. spectral data for Ru(III) Chiral Schiff base complexes

Complexes	λ_{max} ($\varepsilon M^{-1} cm^{-2}$)	$\bar{\nu}$ kK ($\Delta\varepsilon$)
1. Sal-L-Valdichloroaquoruthenate(III)	581(360), 378(1345), 302(1876)	27.6(-1.4), 25.9(+0.38) 22.7(-0.56), 20(+0.49)
2. Sal-L-Argdichloroaquoruthenate(III)	570(162), 386(1131), 305(1800)	30.7(+0.29), 28.9(-0.49) 24.6(+0.49)
3. Salt-L-Hisdichloroaquoruthenate(III)	493(71), 396(96), 336(151), 273(553)	28.9(-0.32), 26.3(+0.28), 20(+0.13), 17.6(-0.12)
4. Sal-L-Aladichloroaquoruthenate(III)	578(259), 368(1082), 345(1297) 326(1302), 306(1305)	27.7(-1.70), 22.4(-0.40), 16.8(+0.30)
5. Sal-L-Methdichloroaquoruthenate(III)	640(525), 389(1480), 347(1645), 296(2053)	27.9(-1.4), 25.9(+0.71), 16.6(+0.13)
6. Sal-L-Aspdichloroaquoruthenate(III)	560(196), 399(1302), 317(157), 301(182)	31.2(+0.25), 26.3(-0.89), 23.5(+0.50), 16.6(+0.20)
7. Sal-L-phealadichloroaquoruthenate(III)	591(204), 347(130), 305(183), 261(2498)	31.2(-1.59), 25.9(+0.23) 16.6(+0.16)
8. Sal-L-cysdichloroaquoruthenate(III)	393(604), 349(117), 303(192)	30.7(+0.20), 28.9(-0.08) 26.6(+0.30)
9. Sal-L-Tyrdichloroaquoruthenate(III)	608(120), 360(864)	31.2(-1.2), 25.6(+0.08) 22.7(-0.08), 14.7(+0.12)
10.Sal-L-Serdichloroaquoruthenate(III)	559(589), 375(1318), 344(1510)	27.7(-1.4), 25.9(+0.68), 23.5(-0.18), 20(+0.36)



R=CH_3, CH_2-C_6H_5, CH_2OH, CH-$(CH_3)_2$, CH_2-S-CH_3, $CH_2C_6H_4$.OH, CH_2-$C_3H_4N_2$, $(CH_2)_3C(NH_2)$=NH, CH_2COOH, CH_2SH

The analytical data and molar conductance of all complexes are listed in Table I. Molar conductivities of the complexes in methanol indicate that they are univalent electrolytes. The magnetic moment μ_{eff} values of these complexes fall in the range 1.98 - 2.07 B.M. indicating the presence of Ru(III) ion with a spin paired $4d^5$ electronic configuration.

A band near 1640 - 1590 cm^{-1} in the infrared spectra of the ligands and complexes may be assigned to the azomethine absorption with an overlap of the υ-COO asymmetric stretching and the C=C/C=N ring stretching bands. This band undergoes a modest decrease in frequency after complexation.[11] The band at 1450 cm^{-1} is assigned to the symmetric υ-COO vibration. The ring stretching vibrations lie at 1354, 1430 and 1475 cm^{-1} in all the complexes. Two additional bands at 1100 and 1170 cm^{-1} along with a broad band at 3400 cm^{-1} appear for all the complexes. These vibrations have been assigned to δ (0-H) and υ (O-H) modes, respectively. Similar observations were made by Ruano et al.[12] The υ (Ru-Cl) and υ (Ru-N) lie near 325-340 cm^{-1}.

The UV-visible spectral data of the complexes are summarised in Table II. The bands near 296 nm and 396 nm may be assigned to $\pi \rightarrow \pi^*$ and $\eta \rightarrow \pi^*$ transitions of the double bond of the azomethine group, respectively. After complexation with ruthenium(III) the band at 396 nm shows a hypsochromic shift which depends on the R group attached to the azomethine group of aminoacid moiety,[6] the energy of the band decreases in the order Sal-Meth > Sal-val > Sal-cys >Sal-ser >Sal-pheala > Sal-Asp > Sal-arg > Sal-ala > Sal-tyro > Sal-his. A moderately intense band near 490 nm can be attributed to the charge transfer transition of the chloride ion. All bands are undoubtedly charge transfer in origin except a band near 640 nm which can be assigned to forbidden ligand field transition of Ru(III).

Two representative circular dichroism spectra for the Ru(III) Schiff base complexes are presented in Figures 1A and 1B. The C.D. data for all the complexes in methanol are summarised in Table II. The C.D. spectra of the two complexes derived from R-(-)-ala (1A) and R-(-)-cys (1B) show that both amino acids have the same absolute configuration in the complexes but R (-) cys is stereospecifically coordinated to the ruthenium moiety so that the gauche chelate ring is located in the δ conformation with very little contribution from the λ isomer while the former complex in solution is in an equilibrium mixture of the conformational isomers (δ and λ) with a preference of λ form. Similar relationships among C.D. spectra were reported elsewhere.[13,6] Thus in all the complexes the steric interaction between substituents at the azomethine carbon and those on the central chelate ring provides the driving force for both the preferred conformation and configuration.

In the ligand field region, 14.7 - 20 kK, CD bands of opposite sign are displayed. This has been assigned to both the d-d bands and spin forbidden ligand bands. As expected an increase in the donor strength of the Schiff base in going from CH_3 to CH_2-R causes a blue shift of the ligand field band.[6] The charge transfer

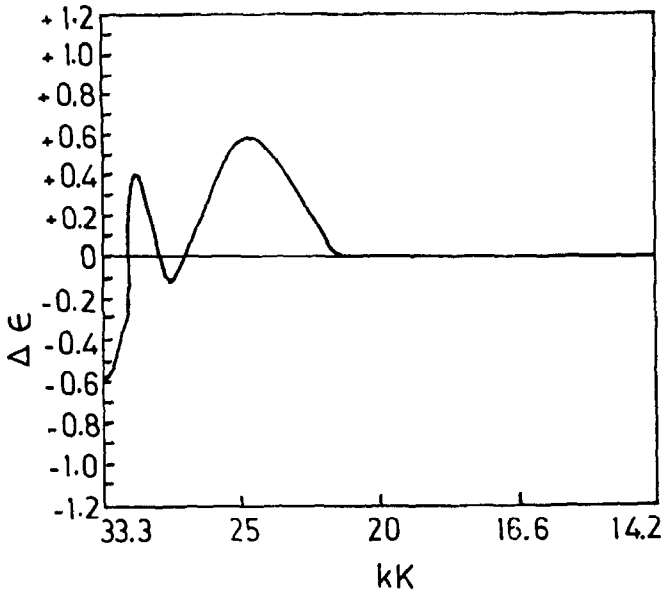


Fig. 1A CD Spectrum of [Sal-L-aladichloroaquoruthenate](III) complex in methanol.

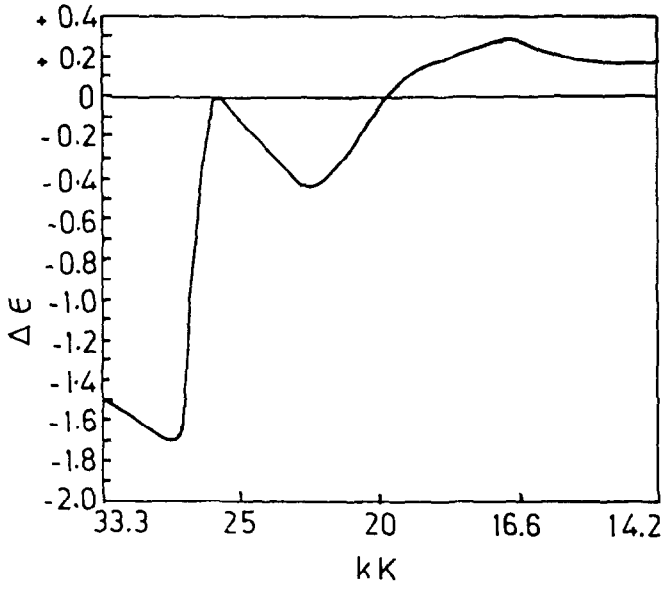


Fig. 1B CD Spectrum of [Sal-L-cysdichloroaquoruthenate](III) complex in methanol.

region of the spectra 22.4 - 26.3 kK indicates a band which can be assigned to d $\rightarrow \pi^*$ azomethine transition. The ligand $\pi \rightarrow \pi^*$ (azomethine) transition band is seen in the higher energy region 27.7 - 31.2 kK. The shift of

both the charge transfer and the ligand transition with azomethine substituents is consistent with the inductive effect of the change of substituent from CH_3 to CH_2-R on the ligand π levels.[14]

Experimental

$RuCl_3.3H_2O$ was from Johnson and Matthey. The compounds salicylaldehyde, L-alanine, L-phenylalanine, L-tyrosine, L-cystein, L-aspartic acid, L-methionine, L-arginine, L-histidine, L-serine, L-valine were from Aldrich Chemicals. The Schiff bases derived from all aminoacids with salicylaldehyde were synthesised by the known procedure.[9] All the complexes were prepared under argon atmosphere. The progress of the reaction were checked by TLC from time to time.

To a hot methanolic solution (1.0 mmol) of the above Schiff base ligands were added (1.0 mmol) of $K_2[RuCl_5(H_2O)]$ in a 1:1 metal:ligand ratio. The reaction mixture was refluxed up to 10-15 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 diethyl ether. The complexes were recrystallised in the same solvent. They were dried in vacuo. Yield 60%.

Microanalyses 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 I.R. spectra were recorded on Carl Ziess Specord M-80 spectrophotometer in Nujol mull/KBr. Electronic spectra were recorded on a Shimadzu UV-Vis recording spectrophotometer model 160. The magnetic moment measurements were made at 298 K by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant and experimental susceptibilities were corrected for dia-magnetism. The optical rotation of the complexes in methanol was measured by polarimeter DIP-360 Jasco Machine. The C.D. spectra were recorded in methanol by Jobin YVON - Paris.

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