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Dirhodium complexes of amino acid derivatives: separation and characterization by circular dichroism spectroscopy

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ABSTRACT

This paper reports on the synthesis and chiroptical spectroscopic characterization of $Rh_2(OAc)_{4-n}$(O-Phe-*Z*)$_n$ (n = 1–4, abbreviated as Rh_2L_1, Rh_2L_2, Rh_2L_3 and Rh_2L_4) complexes. Mixtures of these complexes were prepared in MeCN and $CHCl_3$ solvents from a $Rh_2(OAc)_4$ core complex and the chiral N-protected amino acid *N*-benzyloxycarbonyl-L-phenylalanine (*Z*-Phe-OH). The components of the in situ mixture of complexes proved to be stable enough to be separated by flash chromatography followed by preparative HPLC. The in situ mixtures prepared at different *Z*-Phe-OH to $Rh_2(OAc)_4$ concentration ratios contained different amounts of the Rh_2L_1–Rh_2L_4 complexes. ECD spectra of the individual complexes were measured in MeCN, $CHCl_3$ and EtOH. This is the first time that dinuclear rhodium complexes comprising 1–4 chiral ligands have been characterized by ECD spectroscopy. It was found that the structure of the complexes depends not only on the number of the chiral *Z*-Phe-O $^-$ ligands but also on the donor character of the solvent.

1. Introduction

Dinuclear rhodium(II) complexes have attracted a great deal of attention because of their chemical reactivity,[1] high catalytic activity in many reactions[2–4] and potential applications as anticancer agents.[5,6] It has also been found that a dirhodium complex with Mosher acid ligands can successfully act as a solvating NMR auxiliary for chiral recognition of various monovalent ligands.[7]

Axial ligands, most commonly donor solvent molecules (**D**), are present in the majority of 'paddlewheel' dirhodium complexes (Fig. 1A).[8] Dirhodium tetraacetate $Rh_2(OAc)_4$ can be used as an auxiliary chromophore allowing the determination of absolute configuration of chiral transparent compounds by means of chiroptical studies[9,10]

This is due to the fact that dirhodium tetraacetate can easily exchange in situ one or more of its acetate units with other bidentate ligands to form chiral complexes of a bridging or chelating structure (Fig. 2).[10] Dimolybdenum tetraacetate appears to be the ideal auxiliary chromophore for studying chiroptical properties.[11] However, due to its weak solubility, dirhodium tetraacetate is much more suitable to study the composition of the chiral complexes formed in situ in solution. $Rh_2(OAc)_4$ can accept both mono- and bidentate ligands.[12,13] According to X-ray diffraction data,[1,14,15] $Rh_2(OAc)_4$ has practically ideal D_{4h} symmetry (Fig. 1A, R = CH_3). After ligand(s) exchange, the symmetry of the core remains D_{4h}, since the planar COO^- group(s) should not cause any distortion in the complex geometry, regardless of whether the R group is chiral or achiral. Therefore, the sign of the individual Cotton effects should be determined by sector rules. The simplest sector rule, a hexadecant rule, has been described by Snatzke et al.[16] Amine-ligands first bind in an axial position,[17] but an axial adduct slowly rearranges to give bridging or chelating complexes (Fig. 2A and B). For vic-amino alcohols, a helicity rule was proposed by Frelek and co-workers that links the sign of the Cotton effects above ~300 nm with the sign of the N–C–C–O torsion angle.[10] Low temperature NMR results allowed assignment of the most probable

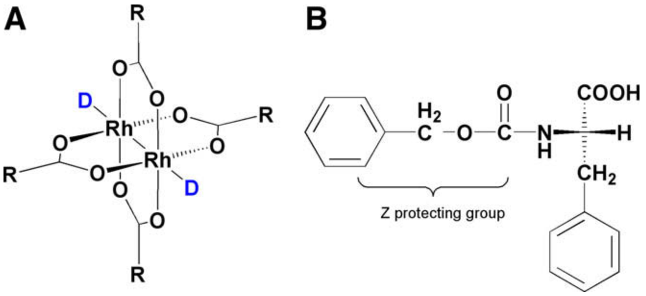

Figure 1. Dinuclear rhodium(II) complexes with carboxylate ligands and axial donor molecules $Rh_2(O_2CR)_4D_2$ (A) and chiral ligand: *N*-benzyloxycarbonyl-L-phenylalanine (*Z*-Phe-OH) (B).

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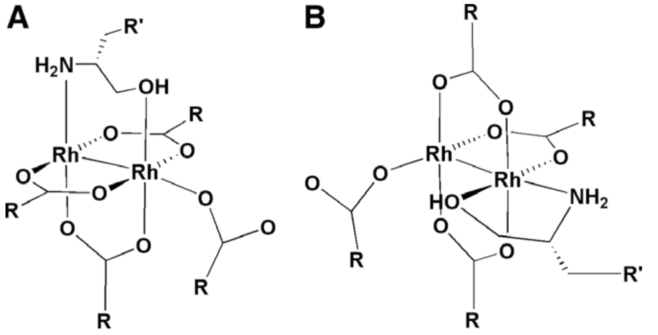

Figure 2. A bridging complex (A) and a chelating complex (B) formed with a chiral vic amino alcohol ligand (redrawn from Ref. 10).

structure of the Rh-complexes with aminols formed in MeCN, $CHCl_3$ and EtOH solutions.[10]

In an attempt to characterize the chiroptical properties of dinuclear rhodium(II) complexes, adducts with *N*-benzyloxycarbonyl-L-phenylalanine (*Z*-Phe-OH, Fig. 1B) were prepared in different solvents and the components of the mixture of $Rh_2(OAc)_{4-n}$(O-Phe-*Z*)$_n$ (Rh_2L_n, n = 1–4) type complexes were separated by HPLC and identified by ESI TOF MS. This paper reports the preparation of the complex mixture, separation and structural characterization of the complexes (n = 1–4) as well as detailed ECD spectroscopic studies on the individual complexes.

2. Results and discussion

2.1. Preparation of the $Rh_2(OAc)_{4-n}$(O-Phe-*Z*)$_n$ type complexes

Our first goal was to investigate the distribution of the $Rh_2(OAc)_{4-n}$(O-Phe-*Z*)$_n$ (n = 1–4) type complexes formed at different ratios of the starting materials. The concentration of $Rh_2(OAc)_4$ was 2 mM, while that of *Z*-Phe-OH was lower or higher than 2 mM. The ratio of different products was determined by analytical HPLC from the area of the peaks. The dependence of the relative integrated intensity of the n = 1–4 complexes on the to *Z*-Phe-OH to $Rh_2(OAc)_4$ ratio is summarized in Table 1. The starting materials were refluxed in dry MeCN for 24 h. At r = 8 (r = [*Z*-Phe-OH]/[$Rh_2(OAc)_4$]) ratio of the starting materials, the main components were the $Rh_2(OAc)_2$(O-Phe-*Z*)$_2$, Rh_2(OAc)(O-Phe-*Z*)$_3$, Rh_2(O-Phe-*Z*)$_4$ complexes (abbreviated as Rh_2L_2, Rh_2L_3 and Rh_2L_4) and an excess of *Z*-Phe-OH. The Fig. 3 shows the analytical HPLC chromatogram of the complex mixture at r = 8 ratio for 24 h boiling time. The separation of the excess of *Z*-Phe-OH from the Rh_2L_1 complex is not simple by HPLC because their retention times are very close.

At r = 0.125 ratio, the main component was the $Rh_2(OAc)_3$(O-Phe-*Z*) (Rh_2L_1) complex in addition to unreacted $Rh_2(OAc)_4$ which was removed by chloroform–water extraction.

$Rh_2(OAc)_4$ went into the water while Rh_2L_1 remained in the organic phase. In this case, the elimination of traces of unreacted *Z*-Phe-OH did not cause any problem.

Table 1
The relative amount (integrated peak intensity) of the complexes formed at different ratios of the starting materials in MeCN (the concentration of $Rh_2(OAc)_4$ was 2 mM)

r	Rh_2L_1	Rh_2L_2	Rh_2L_3	Rh_2L_4
0.125	84.4	15.6	–	–
0.5	40.8	29.4	13.0	16.8
2	37.9	37.5	19.7	4.9
4	13.0	30.6	39.1	17.3
6	4.4	19.0	42.8	33.7
8	3.6	21.3	39.0	36.1

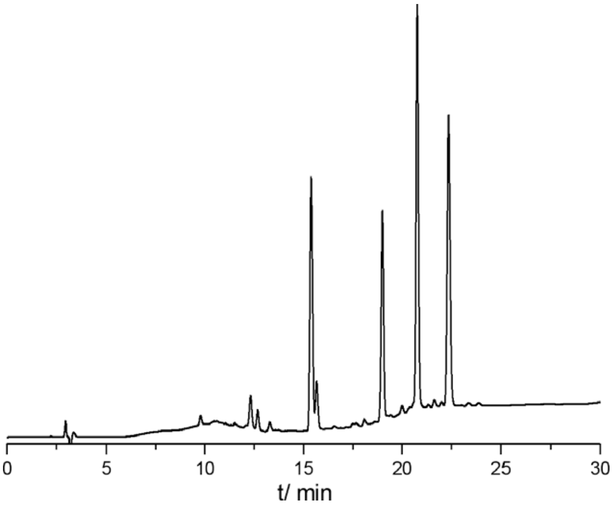

Figure 3. Analytical HPLC chromatogram of the in situ mixture of complexes formed at r = 8. Retention times (t_R): $Rh_2(OAc)_4$, 9.1 min; *Z*-Phe-OH, 15.3 min; Rh_2L_1, 15.6 min; Rh_2L_2, 19.3 min; Rh_2L_3, 20.6 min; Rh_2L_4, 22.3 min.

The Rh_2L_n (n = 1–4) complexes were also prepared in dry $CHCl_3$ at r = 2 ratio. The components reacted at room temperature for 12 h, the main component was the Rh_2L_2 complex.

2.2. Separation of components of the complex mixture

At first, flash column chromatograpy on C-18 silica was used to separate the components of the complex mixture. The eluent mixtures were MeCN and water in different volume percentages (see Section 4). After flash chromatography, the purity of the Rh_2L_1 complex formed at r = 0.125 was 90%, while the Rh_2L_2, Rh_2L_3, Rh_2L_4 complexes obtained at higher r values showed 70–80% purity according to analytical HPLC. The separated components were further purified by preparative HPLC. The complexes were identified by analytical HPLC (Table 2A) and ESI TOF MS. Exact mass measurements yielded information for the confirmation of the dirhodium complexes. Mass accuracy was below 1 ppm in the case of Rh_2L_n (n = 1, 3, 4) complexes (Table 2B). The observed 21 ppm mass deviation for the Rh_2L_2 complex is under further investigation.

Analytical HPLC chromatograms of the isolated complexes are shown in Fig. 4A–D. After the final purification by preparative HPLC, the amount of the isolated Rh_2L_2–Rh_2L_4 complexes was ob-

Table 2A
HPLC characterization of $Rh_2(OAc)_{4-n}$(O-Phe-*Z*)$_n$ complexes

Complexes	Structure	Retention time (t_R), min
Rh_2L_1	$Rh_2(OAc)_3$(O-Phe-*Z*)	15.6
Rh_2L_2	$Rh_2(OAc)_2$(O-Phe-*Z*)$_2$	19.3
Rh_2L_3	Rh_2(OAc)(O-Phe-*Z*)$_3$	20.6
Rh_2L_4	Rh_2(O-Phe-*Z*)$_4$	22.3

Table 2B
ESI TOF MS characterization of $Rh_2(OAc)_{4-n}$ (O-Phe-*Z*)$_n$ complexes

Complexes	Elemental composition	$[M+H]^+$ measured	$[M+H]^+$ calculated	Accuracy (ppm)
Rh_2L_1	$Rh_2C_{23}O_{10}NH_{25}$	681.96631	681.96613	0.26
Rh_2L_2	$Rh_2C_{38}O_{12}N_2H_{38}$	921.04140	921.06076	21.0
Rh_2L_3	$Rh_2C_{53}O_{14}N_3H_{51}$	1160.15480	1160.15539	0.51
Rh_2L_4	$Rh_2C_{68}O_{16}N_4H_{64}$	1399.24920	1399.25002	0.59

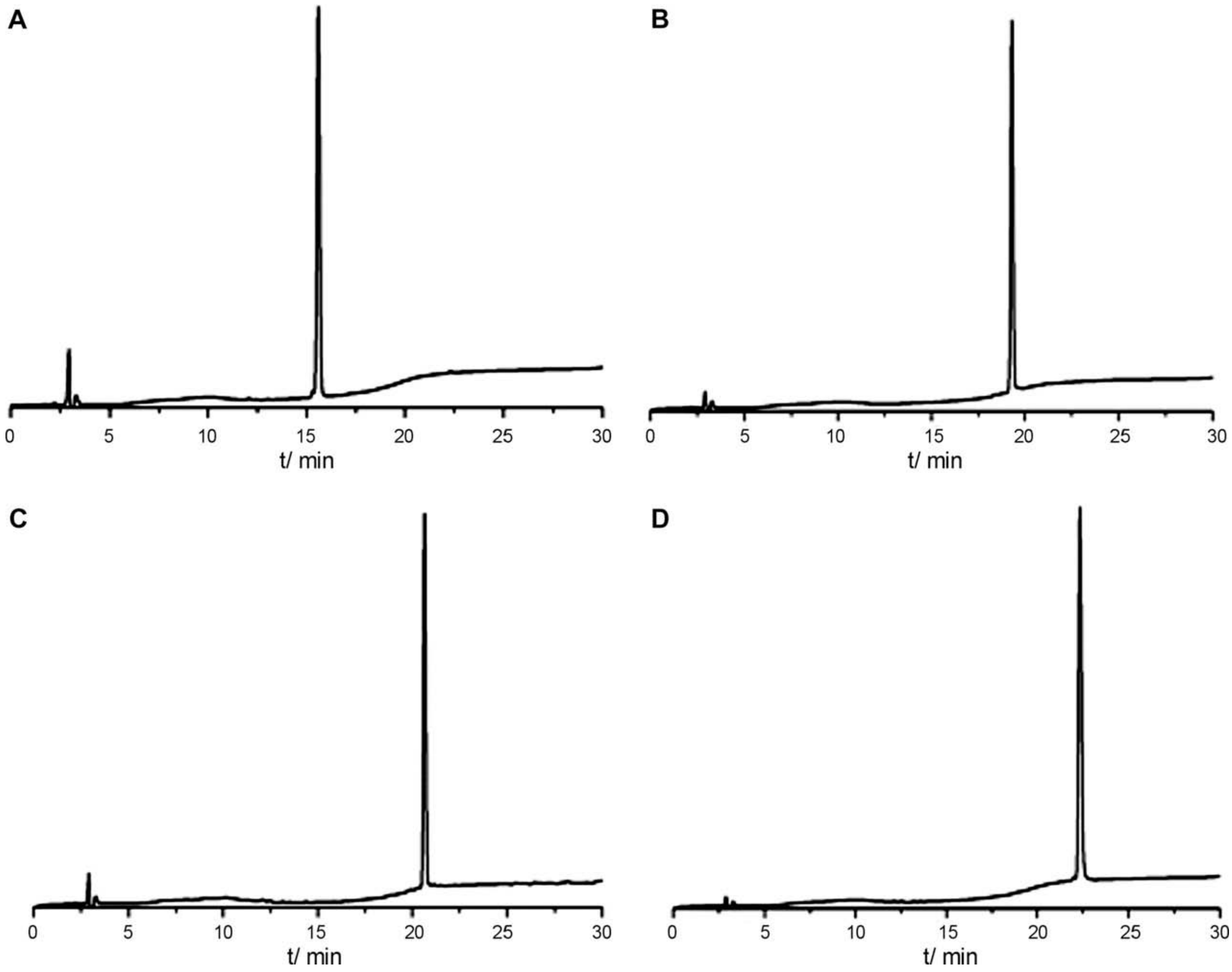

Figure 4. Analytical HPLC chromatogram of the complexes. Chromatogram A: Rh_2L_1, B: Rh_2L_2, C: Rh_2L_3 and D: Rh_2L_4.

Table 3
The amounts of the isolated complexes obtained from a 100 mg prepurified mixture at $r = 0.125$, (Rh_2L_1) and $r = 8$ (Rh_2L_2, Rh_2L_3, Rh_2L_4) in MeCN

Complex	Amount (mg)
Rh_2L_1	7
Rh_2L_2	6
Rh_2L_3	10
Rh_2L_4	8

tained at $r = 8$ in MeCN from 100 mg prepurified mixture and is given in Table 3. The Rh_2L_1 complex was prepared at $r = 0.125$.

2.3. ECD spectroscopy

ECD studies were performed in MeCN, $CHCl_3$ and EtOH. The results of ECD measurements are summarized in Table 4 and Figs. 5–8. The absorption spectrum of $Rh_2(OAc)_4$ in ethanol consists of two weak bands in the visible region, termed band I (at 591 nm) and band II (at 445 nm). In $CHCl_3$, the bands appeared at 607 nm (I) and 425 nm (II), while in MeCN they appeared at 552 nm (I) and 436 nm (II).[10] These bands, attributed to the $\pi^*(Rh–Rh)\rightarrow\sigma^*$ (Rh–Rh) and $\pi^*(Rh–Rh)\rightarrow\sigma^*(Rh–O)$ transitions,[9] respectively, are characteristic of the type of complexes formed because they are strongly influenced by the ligands in axial and equatorial positions. In general, band I is shifted to a lower wavelength depending on the donor character of the axially coordinating ligand(s), while band II is more sensitive to the structure of the equatorial binding ligands.[9] UV–vis spectra of the Rh_2L_1–Rh_2L_4 separated complexes showed in all three solvents that the position of the long wavelength band I remained unchanged. Band II appeared unchanged at 445 nm in EtOH but blue-shifted in the other two solvents (to 444 nm in MeCN and 434 nm in $CHCl_3$).

The ECD spectra of the $Rh_2(OAc)_{4-n}(O\text{-Phe-}Z)_n$ (Rh_2L_1–Rh_2L_4) complexes show 2–5 bands in the 700–300 nm spectral range which are termed A–E in this paper (Table 4).

The bands are of very low intensity in the spectrum of the Rh_2L_1 complex, the shape of the CD curves of the Rh_2L_1 complex is similar in MeCN and $CHCl_3$. Band A is practically not present in the spectra of the Rh_2L_1 and Rh_2L_2 complexes in the solvents used and also in the spectra of the Rh_2L_3 and Rh_2L_4 complexes in MeCN. The spectra of the Rh_2L_2–Rh_2L_4 complexes in MeCN differ significantly from those recorded in $CHCl_3$ and EtOH (Figs. 5–8). The characteristic feature of the spectra in MeCN is a negative band B and a positive band C. Band B above 500 nm becomes more intense in the spectra of the Rh_2L_3 and Rh_2L_4 complexes. In the ECD spectra in $CHCl_3$ and EtOH of the Rh_2L_1–Rh_2L_3 complexes, the position, sign and intensity of bands B and C vary significantly (Table 4). In some cases, these bands are absent or appear only as a shoulder.

In the spectrum in $CHCl_3$ and EtOH of the Rh_2L_4 complex, band B is positive, band C is negative in contrast to their signs in MeCN (Table 4). Bands D and E are negative in all three solvents. In MeCN, band E appears only as a shoulder in the spectrum of the Rh_2L_4 complex.

Comparing the band position and sign pattern of the $Rh_2(OAc)_{4-n}(O\text{-Phe-}Z)_n$ complexes with those of vic-L-phenylalani-

Table 4
ECD data of complexes recorded in MeCN, CHCl$_3$ and EtOH

Complex	Solvent	ECD {Δ*ε* (nm)}*				
		Band A	Band B	Band C	Band D	Band E
Rh$_2$L$_1$	MeCN		−0.02 (506.4)	+0.01 (439.4)	−0.03 (386.6)	−0.04 (331.0)
	CHCl$_3$		−0.05 (507.2)		−0.16 (396.2)	−0.11 (347.4)
	EtOH		+0.02 (521.6)		−0.08 (401.6)	−0.08 (340.2)
Rh$_2$L$_2$	MeCN		−0.06 (503)	+0.04 (441.2)	−0.03 (389)	−0.07 (331.2)
	CHCl$_3$				−0.28 (399.8)	−0.23 (346.0)
	EtOH		+0.02 (511.8)	*sh* (~438.0)	−0.16 (406.2)	−0.16 (341.6)
Rh$_2$L$_3$	MeCN		−0.13 (504.0)	+0.04 (443.2)	−0.06 (391.0)	−0.15 (327.3)
	CHCl$_3$	−0.12 (603.8)		*sh* (~429.5)	−0.44 (406.4)	−0.35 (347.4)
	EtOH	−0.06 (592.8)	+0.01 (516.2)	*sh* (~441.0)	−0.27 (414.2)	−0.24 (344.0)
Rh$_2$L$_4$	MeCN		−0.25 (508.8)	+0.07 (443.2)	−0.06 (390.4)	*sh* (~325.4)
	CHCl$_3$	−0.16 (602.2)	+0.04 (509.4)	−0.57 (429.0)	*sh* (~407.1)	−0.39 (346.8)
	EtOH	−0.14 (586.4)	+0.03 (514.4)	−0.40 (442.6)	*sh* (~406.8)	−0.31 (343.6)

* The *sh* abbreviation means a shoulder.

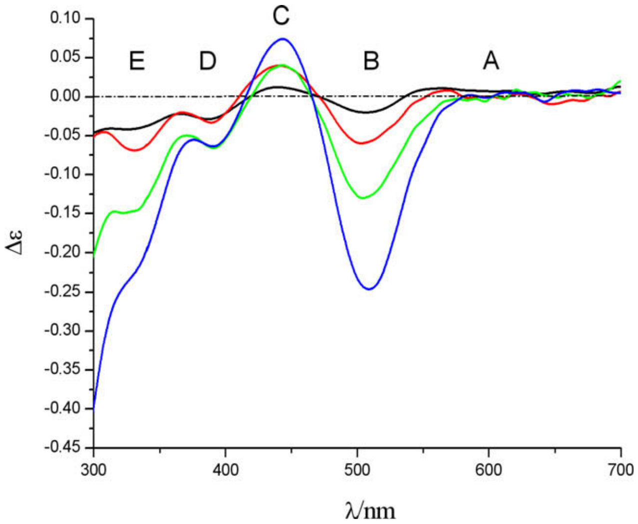

Figure 5. ECD spectrum of the complexes in MeCN, —: Rh$_2$L$_1$, —: Rh$_2$L$_2$, —: Rh$_2$L$_3$, —: Rh$_2$L$_4$.

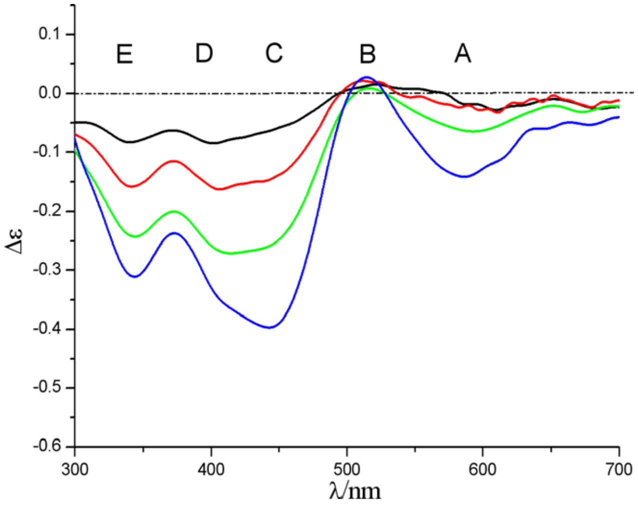

Figure 7. ECD spectrum of the complexes in EtOH, —: Rh$_2$L$_1$, —: Rh$_2$L$_2$, —: Rh$_2$L$_3$, —: Rh$_2$L$_4$.

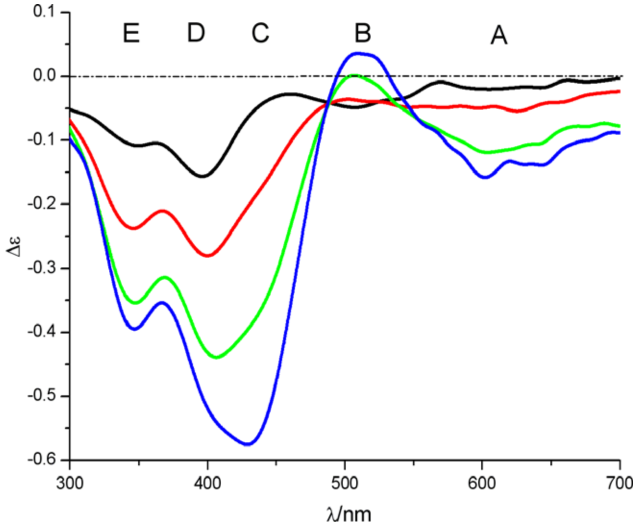

Figure 6. ECD spectrum of the complexes in CHCl$_3$, —: Rh$_2$L$_1$, —: Rh$_2$L$_2$, —: Rh$_2$L$_3$, —: Rh$_2$L$_4$.

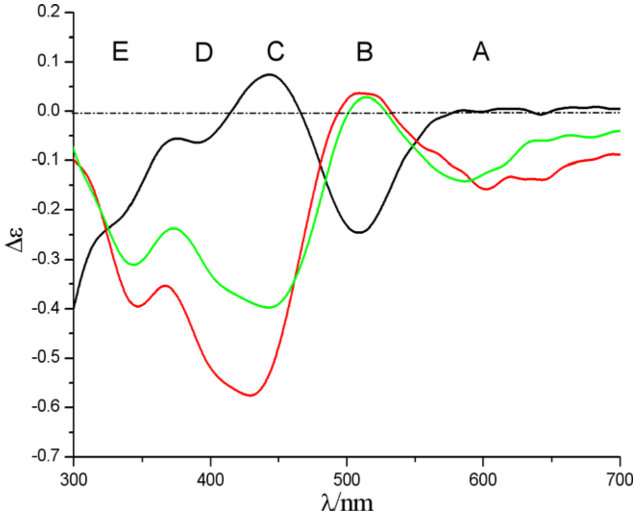

Figure 8. ECD spectrum of the RhL$_4$ in different solvent, —: MeCN, —: EtOH, —: CHCl$_3$.

nol complexes,[17] one can draw the conclusion that the coordination geometry of the dirhodium complexes strongly depends on the structure of the chiral ligands, especially on the softness of the coordinating atoms. According to X-ray crystallographic data, carboxylate ligands prefer to occupy an equatorial position while the N-atom of asymmetric type, N–C–C–OH ligands, can be situated in both equatorial and axial positions.[10] It is reasonable to suppose that the $Rh_2(OAc)_{4-n}(O\text{-Phe-}Z)_n$ complexes bind *Z*-Phe-O^- ligand(s) in both equatorial and axial positions. The COO^- group of *Z*-Phe-O^- may be bound only in bridging position (Fig. 1A) but the coordination of its benzene ring or one of the oxygen atoms of the *Z*-($C_6H_5CH_2$–O–CO–) group in an axial position cannot be excluded. Besides, in the Rh_2L_2 complex the *Z*-Phe-O^- ligands may be situated in a neighbouring or opposite position of the 'paddle-wheel'. Finally, the formation of chains in which the dirhodium complex monomers are attached by the oxygen atoms of the carboxylate and/or the carbonyl of the urethane groups is also possible. This explains the differing spectral features of the complexes which depend on the relative amount of the complex species in solution and their chiral contribution. The size of the substituent(s) attached to the sterogenic centre affects the structure and chiroptical properties of the complexes.[10] The axial donor character of the solvent also plays a significant role in influencing the ECD spectra. The different CD curves in acetonitrile versus ethanol and chloroform may originate from the different types of chiral complexes formed in various solvents. Further studies are in progress to characterize the structure of the $Rh_2(OAc)_{4-n}(O\text{-Phe-}Z)_n$ complexes.

3. Conclusion

In an attempt to characterize the chiroptical properties of dirhodium complexes comprising 1–4 chiral ligands type Rh_2L_n ($n = 1$–4), complex mixtures were prepared from the $Rh_2(OAc)_4$ core complex and *Z*-Phe-OH using different ligand to dirhodium core ratio ($r = 0.125$–8) in MeCN. The components of the in situ mixture of complexes were separated by flash chromatography followed by preparative HPLC.

ECD spectra of the isolated Rh_2L_1–Rh_2L_4 complexes were measured in MeCN, $CHCl_3$ and EtOH. It was found that in MeCN the position and sign pattern of bands B–E were practically the same regardless of the number ($n = 1$–4) of the chiral *Z*-Phe-O^- ligands, only the intensity of the bands increased. It is probable that in solution, the axial positions are occupied by MeCN.

Based on the studies reported herein, the absolute configuration of chiral ligands comprising a carboxylate group can be deduced from the sign of bands B and C in the ECD spectrum of the in situ mixture or the Rh_2L_4 complex measured in MeCN. The CD spectra of the individual complexes in MeCN showed the same shape with different intensities as the measured CD curve using the in situ method at $r = 2$.

It can be concluded that the in situ method, which has been used for the determination of the absolute configuration of chiral vic aminols by Frelek and co-workers can also be applied for the complexes type Rh_2L_n $n = 1$–4.

The structure of the Rh_2L_n ($n = 1$–4) type complexes is uncertain but our ECD studies show that it depends not only on the number of the chiral *Z*-Phe-O^- ligands but also on the donor character of the solvent. Also it has to be noted that in applying this method care must be taken of the N-protected amino acids where the bulkiness or electron donation property of the protecting group with its spectral contribution can cause particular change in CD spectra, even in the sign of Cotton effect. Further studies using chiral *Z*-Ala-OH and Ac-Ala-OH ligands are in progress to obtain more information on the structure of the complexes.

4. Experimental

4.1. Preparation of Rh-complexes

In acetonitrile (MeCN), the complexes were prepared at two different *Z*-Phe-OH to $Rh_2(OAc)_4$ ratios. $Rh_2(OAc)_4$ (221 mg, 0.5 mmol) and *Z*-Phe-OH (18.7 mg, 0.062 mmol, $r = 0.125$ or 1197 mg, 4 mmol, $r = 8$) were dissolved in 250 ml dry MeCN and boiled for 24 h. Formation of the complexes were followed by analytical HPLC. At $r = 0.125$, the main components were the $Rh_2(OAc)_3(O\text{-Phe-}Z)$ and unreacted $Rh_2(OAc)_4$, at $r = 8$ $[Rh_2(OAc)_2(O\text{-Phe-}Z)_2$, $Rh_2(OAc)_1(O\text{-Phe-}Z)_3$ and $Rh_2(O\text{-Phe-}Z)_4$. The solvent was removed by distillation under reduced pressure (evaporated with rotavapour) and the product was a green solid material. In the first case ($r = 0.125$) the green residue was dissolved in 100 ml water and the aqueous solution was extracted with 3 × 30 ml chloroform. The chloroform was removed by distillation under reduced pressure to yield the green solid material $[Rh_2(O\text{-Ac})_3(O\text{-Phe-Z}$, i.e. $Rh_2L_1)]$.

4.2. Separation of the complexes

4.2.1. Pre-purification by flash column chromatography[18]

The load was 5 g C18-silica, 25–40 μm (Lichroprep RP-18, Merck), the column size 1 cm × 25 cm. MeCN (Acetonitril Optigrade®, Promochem) and distilled water in different volume percentages (v/v = 10, 20, 40, 45, 50, 55, 60, 65, 70, 75, 80, 90, 100) were used for elution. The elution was achieved under reduced pressure (20 mm Hg). The mixture of complexes (100 mg) was dissolved in a minimal volume of abs. MeOH and carefully layered on top of the column. The fractions were eluted stepwise with 9–9 ml of the eluents. The eluted liquids were collected in vials after each step. The composition of the mixtures was checked by analytical RP-HPLC. The content of vials comprising mainly the same complex was unified and lyophilized.

4.2.2. High performance liquid chromatography

The analytical HPLC system (Jasco-2000 analytical system) was composed of two pumps (PU-2080), an eluent mixer (MX-2080-31), a photodiode array detector (MD-2010 Plus), an auto injector (AS-2055 Plus), a degasser (MX-2080-54) and a system controller (LC-NetII/ADC). The chromatographic data were recorded by using ChromPass software, version: 1.7.403.1. (all from Jasco, Tokyo, Japan). The preparative HPLC separation was performed with Knauer-64 instrumentation with a fraction collector (CHF 122SB, Adventec). The following chromatographic columns were used:

(1) Agilent C_{18} (4.6 mm × 200 mm), 10 μm (Agilent Technologies, California, US).

(2) Alltech Altima (22 mm × 70 mm), 5 μm (Alltech Associates, Inc., Illinois, Chicago).

(3) Alltech Altima C_{18} (22 mm × 250 mm), 5 μm (Alltech Associates, Inc. Illinois, Chicago).

Analytical HPLC was carried out on column (1), the mobile phase was composed of eluents A and B. Eluent A was bidistilled water containing 0.08% TFA. The bidistilled water was filtered through a membrane filter under reduced pressure. Eluent B contained 95% MeCN, 5% bidistilled water and 0.064% TFA. The flow rate was constant (1.0 ml/min). Gradient elution was applied as follows: 5% B (0 min), 95% B (15 min), 95% B (25 min), 5% B (25.1 min), 5% (30 min). The detection was performed from 220 nm to 600 nm using a photodiode array detector.

The complexes were separated on a preparative column (3) with a precolumn (2) using eluents A and B as mobile phase at a flow rate of 10.0 ml/min, the UV detector was operated at 220 nm. Eluent A was 50% bidistillated water and 50% MeOH

(Chromasolv®, Sigma Aldrich) with 0.1% TFA and eluent B, MeCN with 0.08% TFA. Gradient elution was used as follows: 5% B (0 min), 95% B (15 min), 95% B (30 min). Fractions containing the pure Rh_2L_1–Rh_2L_4 complexes according to analytical HPLC were combined and lyophilized to yield greenish powders.

4.2.3. Mass spectrometric analysis of purified dirhodium complexes

An Agilent Technologies 1200 series LC system equipped with a binary pump (G1312A) and a standard autosampler (G1229A) was used for the flow injection analysis (FIA). Mobile phase A was deionized water with 0.2% (v/v) formic acid, mobile phase B was gradient grade methanol (Merck). Isocratic condition was employed with 50% mobile phase B at a flow rate of 0.4 ml/min. Mass spectrometric detection was carried out using an Agilent 6210 Time-of-Flight mass spectrometer. The instrument was operated using a dual-nebulizer electrospray ionization source (ESI) in positive mode. Source conditions were as follows: drying gas flow = 8.0 L/min N_2, nebulizer = 35 psig N_2, drying gas temperature = 350 °C, capillary voltage = 4000 V. Fragmentor voltage was 170 V. The purified dirhodium complexes were reconstituted with methanol–water (1:1) solution and analyzed by FIA. Two reference masses (*m*/*z* 121.050873,922.009798) were used to recalibrate the mass axis during the analysis. Full scan mass spectra were acquired over an *m*/*z* range of 100–1600 and processed by the Agilent MASSHUNTER software for the individually injected samples. In all cases, the positive ion mass spectrum consisted mainly of the intense protonated molecular ion $[M+H]^+$ and the sodium adduct $[M+Na]^+$, but complexes also gave a less intense dimer peaks corresponding to $[2M+H]^+$ and $[2M+Na]^+$. For the confirmation of the complexes, the measured masses of the protonated molecular ions were compared with the calculated theoretical values.

4.3. Electronic circular dichroism spectroscopy

ECD measurements were performed on a Jasco J-810 spectropolarimeter. ECD spectra were recorded in the 300–700 nm range at room temperature in different solvents (MeCN, $CHCl_3$ and EtOH) in 10 mm path length quartz cell. The following parameters were used: spectral band width 1 nm, response time 0.5 s, continuous scanning, data pitch 0.1 nm, scanning speed 50 nm/min, accumulation 2. Before the measurements, the samples were dried in vacuum desiccator for 12 h above phosphorpentoxide. For CD measurement, the solid chiral (Rh_2L_n $n = 1$–4) complexes (ca. 1–3 mg, 0.001 mol/L) were dissolved in the solvent.

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