Turkish Journal of Chemistry

Volume 32 | Number 2 Article 11

1-1-2008

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Turk J Chem
32 (2008) , 237 – 247.

Synthesis and X-Ray Structural Studies of Amino Acids Half Sandwich Complexes of Osmium(II)

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Received 14.09.2007

The amino acids complexes of osmium(II), i.e. [Os(η6-p-cymene)(η1-N-(rac)-phenylglycine methyl ester)Cl_2] (**A**) and [Os(η6-p-cymene) (η1-N,N'-(S)-phenylalanine amido) Cl] (**B**), were prepared by an ultrasound energy-assisted method at room temperature. The solid structures of the newly synthesized complexes were determined by single crystal X-ray analysis. In **A,** osmium is bonded to 2 chloride ligands, the η6-coordinated p-cymene molecule, and to a nitrogen atom of the corresponding amino acid derived ligand, whereas in the case of **B** the central osmium is surrounded by an N, N' bidentate amino amide ligand, by an η6-coordinated p-cymene molecule, and a chloride ligand. Both complexes have a pseudo-tetrahedral geometry. As shown by X-ray structure, **A** exhibited racemization of the corresponding ligand. The ligand retained its configuration in **B** with co-crystallization of the 2 diastereomers, $R_{Os}S_C$ and $S_{Os}S_C$, in a single crystal.

Key Words: Osmium; X-Ray studies, N ligands, Amino acids, Half sandwich Complexes

Introduction

Transition metals, such as Rh, Pd, Pt, Ru, etc., have been extensively used as heterogeneous catalysts[1−2] for various transformations of molecules. A great number of transition metal complexes have been prepared and used as homogeneous catalysts,[3−4] because they are considered intermediates of metal-catalyzed reactions.

In general, not much is known about the chemistry of osmium arene complexes compared to those of iron and ruthenium. Ruthenium and platinum complexes that contain chelating N,N-heterocyclic ligands, for example, phenanthroline (phen), bipyridine (bipy), and phenylazopyridine (azpy), have been extensively studied and some have been reported to show anticancer activity.[5−7]

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The extensive use of amino acids and their derivatives as ligands is an extensively-researched topic in organometallic chemistry.[8] Metal complexes involving amino acid-type ligands have applications mainly in bio-inorganic chemistry, for example, in the synthesis of peptides[9] or bio-inorganic models.[10]

In this paper we report the synthesis and characterization, and the spectroscopic and X-ray structure analysis of 2 new half-sandwich osmium(II) complexes, which were obtained using (R)-phenylglycine methyl ester (**L1**) and (S)-phenylalanine amide (**L2**) as ligands. Analysis of the anticancer activity and catalytic behavior of the reported complexes are currently underway in our laboratories.

Experimental

General methods

All of the reactions were performed under an atmosphere of dry nitrogen, using standard Schlenk techniques. Solvents were dried before use and were stored over molecular sieves under nitrogen. Elemental analyses (C, H, and N) were performed using a Flash EA 1112 analyzer. Infrared spectra were recorded with a Nicolet 5700 FT-IR spectrophotometer in the range of 4000-400 cm^{-1}. 1H NMR spectra were obtained at 300 K on a Bruker 300 FT spectrometer, using $SiMe_4$ as the internal standard. The hydrochloride forms of enantiomerically pure (R)-phenylglycine methyl ester (L1.HCl) and S-phenylalanine amide (HL2.HCl) were purchased from Aldrich, while $[Os(p\text{-cymene})Cl_2]_2$ was synthesized according to the literature.[11] Acetophenone (Aldrich) and cyclohexanone (Fluka) were used as received.

Preparation of the Os(II) Complexes

[Os(η6-p-cymene)(κ 1-N-L1)Cl_2] (A)

In 30 ml of ethanol, 198 mg (0.9 mmol) of L1.HCl and 100 mg (0.9 mmol) of t-BuOK were dissolved at room temperature; n-pentane was added and KCl was filtered-off. A chloroform solution (15 ml) of $[Os(p\text{-cymene})Cl_2]_2$ (475 mg, 0.5 mmol) was added and the resulting dark brown solution was put in an ultrasonic bath at room temperature for 1 h. A brown solid precipitated, which was filtered-off, washed with diethyl ether, and dried in vacuum. A further yield of solid was obtained from the refrigerated mother liquor. Brown crystals suitable for X-ray analysis were obtained by re-crystallization in ethanol. Yield: 298 mg (79%); mp: 188 200 °C. 1H NMR ($CDCl_3$): d 1.29 (d, 3H, p-cymene, 3JHH = 7Hz), 1.35 (d, 3H, p-cymene, 3JHH = 7 Hz), 2.18 (s, 1H, $H(Ph)NH_2$), 2.27(s, 3H, p-cymene), 3.10 (m, 1H, NH), 2.91 (m, 1H, p-cymene), 3.75 (s, 3H, $(O)OCH_3$), 5.26(d, 1H, p-cymene, 3JHH = 6 Hz), 5.31(d, 1H, p-cymene, 3JHH = 6 Hz), 5.45 (m, 2H, p-cymene), 7.40 (m, 5H, Ph), 7.69 (m, 1H, NH). Anal. calc. for $C_{19}H_{23}Cl_2$- NO_2Os: C, 40.71; H, 4.50; N, 2.50%. Found: C, 40.47; H, 4.59; N, 2.66%. IR: 3274-3221-3149 m(NH_2), 1739 m(C=O ester), 1258 m(C=O ester).

[Os(η6-p-cymene)(κ2-N,N'-L2)Cl].1/2H_2O (B)

In 30 ml of ethanol, 130 mg (0.6 mmol) of HL2.HCl and 67 mg (0.6 mmol) of t-BuOK were dissolved, a chloroform solution (15 ml) of $[Os(p\text{-cymene})\text{-}Cl_2]_2$ (252 mg, 0.3 mmol) was added, and the resulting brownish solution was agitated in an ultrasonicator at room temperature for 1 h. The solvents were then removed (in vacuum) and the residue was treated with chloroform, filtering the KCl off. The remaining

light brown solution was refrigerated at 5-8 °C to obtain brown prismatic crystals. A further yield of solid (orange powder) was obtained by treating the mother liquor with diethyl ether after filtration. Yield: 262 mg (75%); mp: 241-245 °C. 1H NMR (CD_3OD): major diastereomer d 1.25 (d, 3H, p-cymene, 3JHH = 7Hz), 1.34 (d, 3H, p-cymene, 3JHH = 7Hz), 2.08 (sbr, 1H, NH), 2.11 (s, 3H, p-cymene), 2.44 (m, 2H, CH2), 2.73 (m, 1H, p-cymene), 3.10 (dd, 1H, CH(Bz)NH_2, 2JHH = 4.3 Hz), 5.54 (d, 1H, p-cymene, 3JHH = 6Hz), 5.63 (d, 1H, p-cymene, 3JHH = 5.8 Hz), 6.14 (d, 1H, p-cymene, 3JHH = 5.8 Hz), 6.48(d, 1H, p-cymene, 3JHH = 6Hz), 7.32–7.09 (m, 7H, Ph + NH_2); minor diastereomer d 1.16 (d, 3H, p-cymene, 3JHH = 6.9 Hz), 5.20 (dbr, 2H, p-cymene, 3JHH = 5.7 Hz), 5.41 (dbr, 2H, p-cymene, 3JHH = 4.7 Hz). Anal. calc. for C19H25ClN2OOs.1/2H2O: C, 42.89; H, 4.93; N, 5.26%. Found: C, 42.65; H, 4.74; N, 5.41%. IR: 3288–3120 (NH), 1580(C=O amide).

X-Ray Structures

X-ray diffraction data were collected on a Bruker-Siemens SMART AXS 1000 equipped with a CCD detector, using graphite monochromated Mo K_α radiation (λ= 0.71065` Å). Data collection details were as follows: Crystal to detector distance: 5.0 cm; frames collected: 2424 (complete sphere mode); time per frame: 30 s; oscillation D U: 0.300°. Crystal decay was negligible in both cases. Data reduction was performed for **A** and **B** up to d = 0.70 and 0.90Å, respectively, with the SAINT package,[14] and data were corrected for absorption effects using the SADABS[15] procedure (T_{max} = 1.000 and T_{min} = 0.788 for **A,** and T_{max} = 1.000 and T_{min}

Table 1. Coordination bond lengths (Å) and angles (°) for A and B.

A:

S. No.	Bonds	Bond Lengths	Bonded Atoms	Angles
1	Os–N	2.162(1)	N–Os–Cl2	82.19(4)
2	Os–(C10–C15)	2.153(1)–2.200(1)	N–Os–Cl1	82.07(4)
3	Os–Cy	1.61	Cl2–Os –Cl1	87.11(1)
4	Os–Cl2	2.4136(4)	Cy–Os–N	133
5	Os–Cl1	2.4203(4)	Cy–Os–Cl1	125
	—	—	Cy–Os–Cl2	128

B:

S. No.	Bonds	Bond Lengths	Bonded Atoms	Angles
1	Os1–N1	2.055(9)/ 2.123(8)	Os2–N3	2.050(9)
2	(C10–C15)	2.15(1)–2.19(1)	Os2–(C29–C34)	2.13(1)–2.24(1)
3	Os1–Cl1	2.432(3)	Os2–Cl2	2.435(3)
4	Os1–Cy1	1.62	Os2–Cy2	1.67
5	N1– Os1–N2	76.5(3)	N3– Os2–N4	76.5(3)
6	N1– Os1–Cl1	86.3(3)	N3– Os2–Cl2	87.5(3)
7	N2– Os1–Cl1	82.5(2)	N4– Os2–Cl2	82.3(3)
8	Cy1– Os1–N1	130	Cy2– Os2–N3	131
9	Cy1– Os1–N2	131	Cy2– Os 2–N4	132
10	Cy1– Os1–Cl1	127	Cy2– Os2–Cl2	128

Table 2. Crystal data and structure elucidation for **A** and **B.**

Identification code	A	B
Empirical formula	$C_{19}H_{25}Cl_2NO_2Os$	$[C_{19}H_{25}ClN_2OOs]_2{\cdot}1/2H_2O$
Formula weight	560.00	1054.00
Wavelength (A°)	0.71069	0.71069
Crystal system	triclinic	tetragonal
Space group	P	$I4_1$
Unit cell dimensions		
a (Å)	9.7090(9)	23.551(2)
b (Å)	9.7698(9)	
c (Å)	10.765(1)	14.721(1)
α (^{o})	97.615(2)	
β (^{o})	97.412(2)	
γ (^{o})	105.011(2)	
Volume (Å^3)	965.92(15)	8190(1)
Z	2	8
D_{calc} Mg/m^3	1.6154	1.425
Absorption coefficient mm^{-1}	1.0995	0.907
F (000)	480	3595
θ Range for data collection (^{o})	1.93-30.33	1.51-24.01
Reflections collected	13591	36800
Data/restraints/parameters	5256/0/240	5920/9/440
Goodness-of-fit on F2	1.3036	1.171
Final R indices [I > 2r(I)]	R_1 = 0.0210, wR_2 = 0.0531	R_1 = 0.0361, wR_2 = 0.9981
R indices (all data)	R_1 = 0.0240, wR_2 = 0.0551	R_1 = 0.0539, wR_2 = 0.1202
Largest dF maximum/minimum (e Å $^{-3}$)	0.485/-0.459	0.912/-0.310

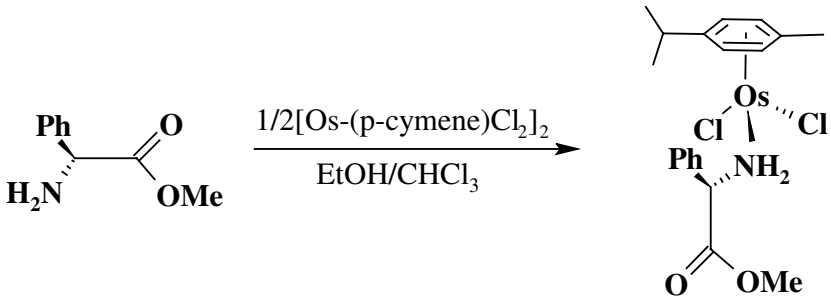
= 0.848 for **B**). The phase problem was solved by direct methods and refined by full-matrix least-squares on all F21,[16] implemented in the WINGX [19] package. A partially occupied (50%) water molecule completes the asymmetric unit contents for **B**. The absolute structure for **B** was assessed by Flack's parameter = –0.10 (7). Anisotropic displacement parameters were refined for all non-hydrogen atoms, while hydrogen atoms were introduced in calculated positions, leaving only amine and amide hydrogen atoms, which were positioned from Fourier maps and then refined isotropically. Refinement results and data collection are also reported (Table 2). Cambridge Crystallographic Database[19] facilities were used for complete structure discussion.

Results and Discussion

In an ethanol/chloroform mixture, $[Os(p\text{-cymene})Cl_2]_2$ was made to react with L1.HCl at room temperature to yield complex **A** (Scheme 1). The reaction was conducted under dry conditions to avoid the hydrolysis of the methyl-ester group of the corresponding ligand. **A** was obtained as a brownish powder, which is stable, both in the solid state as well as in open air solution form, with a pseudo-tetrahedral geometry, where

osmium is bonded to an η6-coordinated p-cymene molecule, to the amine group of L1, and to 2 chloride ligands.

The ester group remains out of the coordination sphere, which was evidenced by the strong IR stretching band at 1739 cm^{-1}, equivalent to that of L1.HCl. The stretching signals of the amine group are in the range of 3267-3148 cm^{-1}. In the 1H NMR spectrum, the splitting of the NH_2 signals (2 multiplets at 3.06 and 7.05 ppm, respectively) was obvious as a result of the interaction of the nitrogen donor with the metal center. Moreover, all other signals showed the expected chemical shifts.



Scheme 1.

Very fine single crystals of **A** were grown in ethanol to establish the structure of the complex. The crystal structure of **A** (Figure 1) suggested that the coordination geometry of the [$OsNCl_2(\eta6\text{-}C_6)$] moiety (Table 1) was tetrahedral, by considering the center (Cy) of the η6-p-cymene aromatic ring being in the fourth ligand position. In fact, the Os–C distances relative to the p-cymene coordination range from 2.167 Å (±0.002) (for **B**) to 2.200 Å (±0.002) (for **A**), with Os–Cy = 1.659 Å (±0.002) (for **A**). The overall shape of **A**, therefore, may be called a piano stool-like geometry. The racemization of L1 may be due to the presence of a phenyl ring on the a-carbon atom, which is able to stabilize the incipient carbo anion[20] formed upon proton abstraction enhanced by traces of free t-BuOK. This is supported by the unobserved racemization of the ligand during the synthesis of a similar ruthenium [Ru(η6-benzene)(L-alaMe)Cl_2] complex,[21] where a methyl group is attached to the a-carbon atom.

The significant distortion in the tetrahedral coordination geometry, by tightening of the N–Os–Cl angles, and the widening of those of Cy–Os–N and Cy–Os–Cl is clearly a function of the large steric hindrance of p-cymene. The p-cymene is positioned in such a way that the C10–C16 bond to the methyl group is eclipsed to the Os–Cl2 bond [C16–C10–Os–Cl2 = 11.3(2)°]. The most pertinent conformational degrees of freedom of L1 in **A** are the rotations around the Os–NH_2 bond and the NH_2–CH bond, which together determine the orientation of the aromatic group of the phenylglycine residue relative to the p-cymene ligand. As regards the former, in **A** the N–H bonds belonging to the mono-hapto –NH_2 group are eclipsed with respect to the Os–Cl bonds (Cl2–Os–N–C1 = 126.2(1)°), while the latter is characterized by the torsion angle, Os–N–C1–C2 = 60.2(2)°. These values show that the ligand aromatic residue is oriented towards the p-cymene methyl end, giving edge-to-face intramolecular contact between the p-cymene aromatic C–H groups and the L1 π electron density (H11—- C2 = 2.67 Å (±0.002)). In examining the crystal packing of **A** it is convenient to refer to the distribution of the shortest Os–Os contacts in order to analyze how the complex molecules are paired by intermolecular interactions (Table 3). Brunner individuated the inverted piano stool motif as a common molecular recognition pattern in (p-cymene)MXYZ-type complexes. In particular, this motif has been invoked to justify the remarkable trend to co-crystallization shown by the diastereoisomeric pairs,[22] and this issue will be further considered in discussing the crystal structure of **B**.

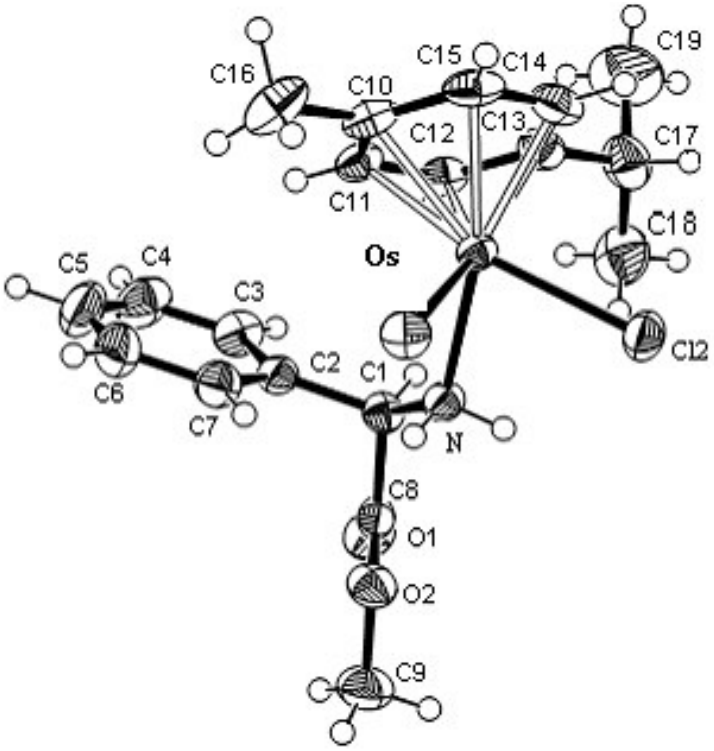


Figure 1. The molecular structure of **B** and its atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

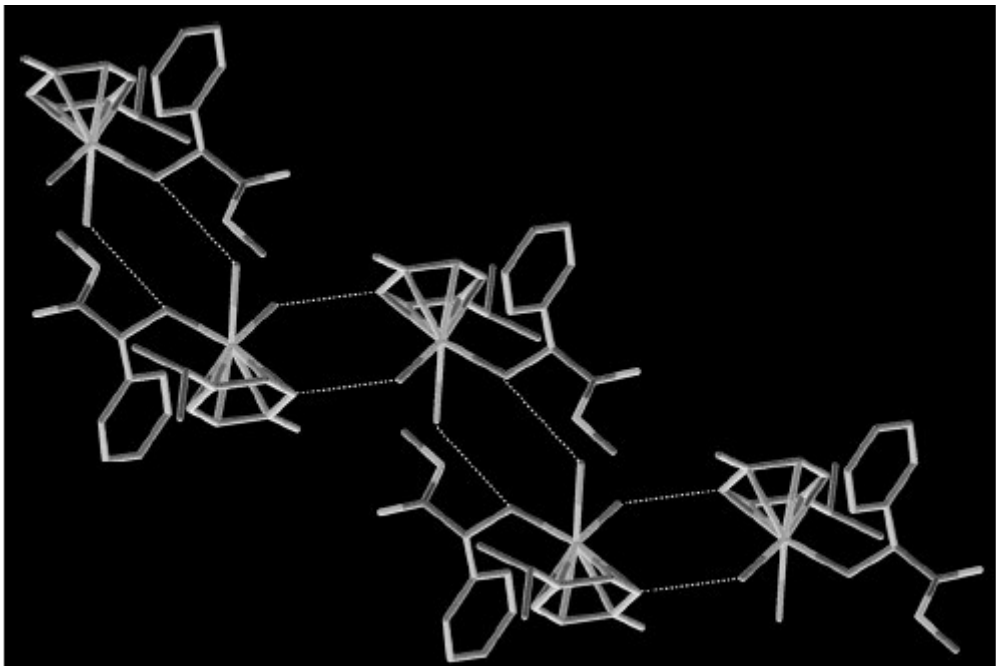


Figure 2. Molecular aggregation with hydrogen bonding in the crystal structure of **A**.

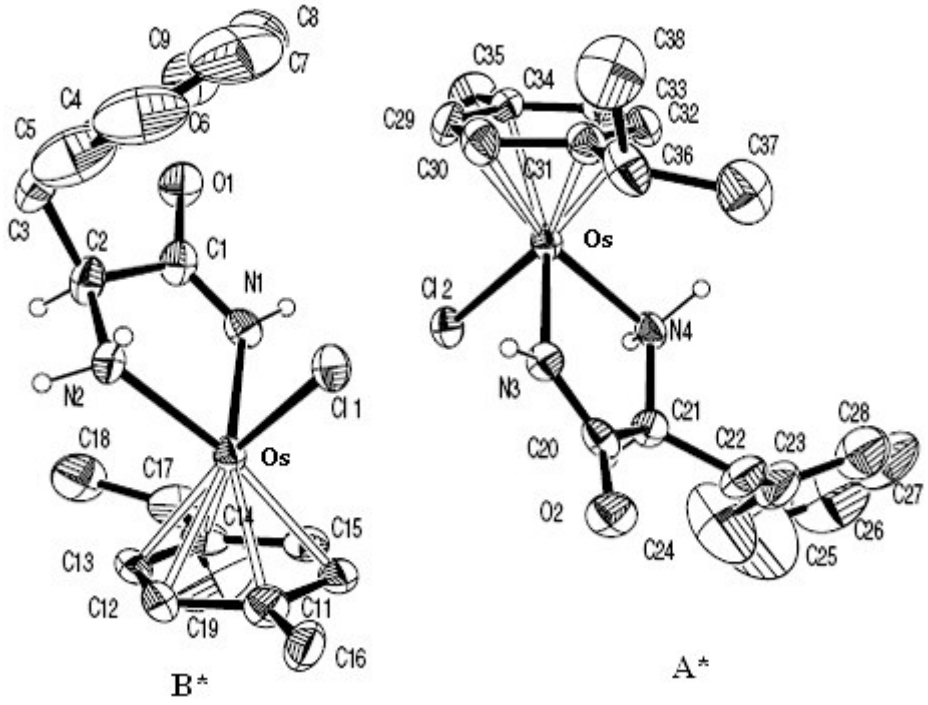


Figure 3. The molecular structure of **A** and **B** and their atom-numbering schemes. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen not bonded to N and chiral C atoms have been omitted for clarity.

Table 3. Hydrogen-bond geometry for **A** and **B.**

A:

Bonds	Bond lengths (`Å)	Bonded atoms	Angles (°)
Os-Os i	6.65	Cy-Os-Os i	76
Os-Os ii	6.77	N-H—Cl ii	145(2)
N-Cl ii	3.51 (2)	C-H—Cl2 i	30(2)
-NH—Cl i	11.51 (2)	C=O—H i	129
-NH—Cl ii	10.25 (2)		

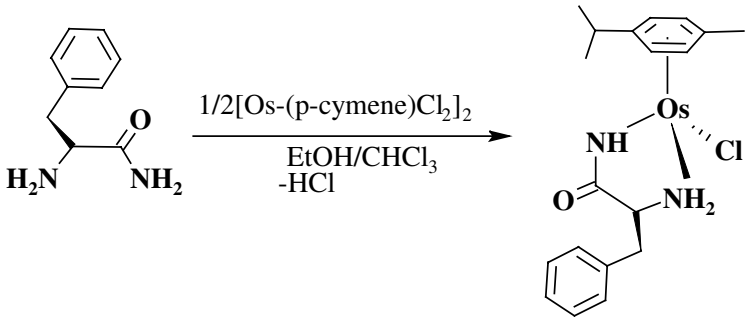
B:

Bonds	Bond lengths (`Å)	Bonded atoms	Angles (°)
-N2—O1 i	2.78(1)	N2-H—O1 i	164(7)
-N4—O2 ii	2.84(1)	N4-H—O2 ii	161(6)
-N1H—Cl2 i	2.64	C-H—O1 i	42(2)
-N3H—Cl1 ii	2.54	N3—Cl—CH(Cy)	64(n)

[Symmetry codes: (i) $-x_1$-y_1 2-z , (ii) $-x_1$-y_1 1-z]

HL2 reacts with $[Os(p\text{-cymene})Cl_2]_2$ under the same experimental conditions as for **A**, leading to complex **B** (Scheme 2). The product is stable in the solid state as well as in open air solutions. The ligand shows bidentate behavior, binding the metal through the amine and amide nitrogen atoms. Complexation occurs with elimination of an HCl molecule, subsequent to the mono deprotonation of the amide nitrogen,

and then L1 acts as an anionic N,N' bidentate ligand. The pseudo-tetrahedral coordination is completed by a chloride ligand and an η6-coordinated p-cymene ring. The IR spectrum shows a strong stretching band of the amide C=O group at 1575 cm^{-1},[23,24] while the stretching of the NH bonds originates in an unresolved band in the region of 3280-3120 cm^{-1}. The 1H NMR spectrum recorded in CD_3OD shows the presence of 2 diastereomers (see Section 3); at room temperature they are in a 75:25 ratio. The formation of pairs of diastereomers is common for half-sandwich Os(II) complexes of this type that contain chiral bidentate ligands; in complexes of the general formula, M(arene)(LL')X (X = halogen or other unidentate ligand), the formally monohapto coordination of the p-cymene ring imparts the metal a stereogenic center. Thus, in the presence of an enantiomerically pure ligand (in the present case having an S_C configuration), the 2 diastereomers, $R_{Os}S_C$ and $S_{Os}S_C$, appear.



Scheme 2.

Interestingly, the X-ray diffraction analysis carried out on a single crystal of **B** obtained from a chloroform solution at 5 °C showed the presence of both diastereomers. In contrast to ligand L1, the X-ray analysis of **B** indicates that L2 has retained its configuration at the stereogenic carbon atom. The presence of 2 diastereomers in the same crystal is an interesting feature, already observed for ruthenium and a congener of osmium in Ru(η6-arene)(LL')Cl-type complexes; more than 17 examples are reported in the literature,[22] the majority of which deal with the type of complexes of the general formula, [Ru(η6-p-cymene)(salicylaldiminate-ligand)Cl], and only in one case the ligand is N,N'[22]. This co-crystallization is usually based on a sort of molecular recognition within inverted piano stool-like dimers. This feature is evident in the crystal structure of the 2 independent diastereomers, $S_{Os}S_C$ (molecule A*, Os2) and $R_{Os}S_C$ (molecule B*, Os1), present in the asymmetric unit of **B**.

Table 1 lists the most similar geometric characteristics of the 2 molecules, which co-crystallize in the acentric polar space group, $I4_1$. In both cases, the osmium coordination is tetrahedral, by considering the chlorine ligand, the amidic and aminic nitrogen atoms of the bidentate ligand, and the geometric centre (Cy) of the p-cymene aromatic ring as the 4 donors. In both molecules, the coordination to the deprotonated amidic donor is stronger than the aminic group. The N, N' chelation of L2 to Os generates a 5-membered chelation ring, with bite angles N– Os –N = 76.5(3)°, in A* and B*, while the remaining coordination angles on Os are larger than the corresponding ones in A*. The opposite absolute configuration of the metal in A* and B* results in a different orientation of the Os –Cl bond relative to the C–H bond of the chiral carbon atom (C2 and C21, respectively, for A* and B*). Both bonds are axially oriented with respect to the chelation rings, but they are in anti-configuration in B* and syn-configuration in A*. The p-cymene is always coordinated with the methyl end pointing towards the chlorine ligand [C16–C11– Os1–Cl1 = –20.6(9)°, C16 – – – Cl1 = 3.55(1) Å ; C35–C34– Os2–Cl2 = –23.5(9)°,C35 – – – Cl2 = 3.56(1) Å]. Diastereomers A*

and B* co-crystallize by forming an inverted piano stool dimer, wherein A* and B* are related by a non-crystallographic operation mimicking a center of inversion, so that the aromatic p-cymene moieties lie parallel on opposite sides relative to the metal atoms. It has been suggested[22] that the stability of this inverted piano stool recognition pattern is the reason for the relevant occurrence of diastereomers co-crystallization for Os(η6-arene)XYZ-type complexes with electronegative X and Y. The inversion operation is required in order to create contacts between complementary groups on A* and B*: C29—O1 = 3.41(1), C10 – – – O2 = 3.36(1), N1– – – Cl2 = 3.490(8), and N3 – – – Cl1 = 3.481(8) Å. This non-crystallographic operation acts locally between the metal centers of the A*–B* dimers, so that the 2 molecules show opposite chirality on the metals.

However, due to the enantiomeric purity of L2, the symmetry relation cannot be extended to the entire molecular pair, but is confined to the central core, inside the limit defined by the chiral carbons. The 2 resulting $S_{Os}S_C$ and $R_{Os}S_C$ complexes are in close contact, with Os1 – – – Os2 = 5.11 Å (±0.002), Cy– Os– Os– Cy' = 180° (±0.002), and Cy– Os– Os' = 111°(±0.002), which are quite typical values for this kind of pattern.[12] The next shortest Os – Os' contacts are larger than 6.6 Å (±0.002). Most interesting is the organization of the crystal architecture. Each diastereomer is part of a helix of analogous molecules based on the strong hydrogen bonds (Table 3). Both helices **A** and **B** are generated by the 4_1 symmetry operator, with pitch c = 14.572(1) Å (Figure 4), but they have opposite handedness; right-handed for B and left-handed for A. The helix handedness is governed by metal configuration, so that all the chlorine ligands stick out from the corners of the chains. The intra-chain packing of L2 is the main difference between the 2 diastereomeric helices, A and B. Helices interact in the crystal through the inverted piano stool dimers located at each 90° turn of the helix, so that each helix is surrounded by 4 helices of opposite type packed in anti-parallel mode.

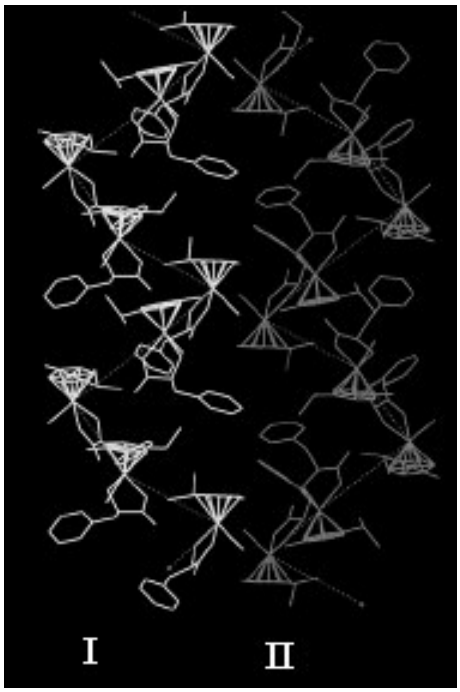


Figure 4. Different 3D orientations and structures of the hydrogen-bonded chains in **B**. The opposite handedness of the chains formed by **I** (left handed) and **II** (right handed) is represented by a dotted line connecting the Os atoms.

The preparation of Os(II) complexes containing other amino acids ligands with the aim to improve the enantioselectivity of the hydrogen transfer reaction, as well as their anticancer activity, is currently being carried out in our laboratory.

Conclusions

Os(II) complexes of amino acid derivatives were prepared and characterized. X-ray studies were carried out to establish the crystal structure of both complexes. Atypical co-crystallization of the 2 diastereomers, $R_{Os}S_C$ and $S_{Os}S_C$, was found in complex **B**, with the ligand, (S)-phenylalanine amide. The 2 helices have opposite handedness defined by the metal configuration; left-handed for the $R_{Os}S_C$ isomer and right-handed for the $R_{Os}S_C$ isomer.

Acknowledgment

Special thanks are due to HEC (Higher Education Commission) of Pakistan for junding this entire project.

References

1. P. McMorn and G. J. Hutchings, **Chem. Soc. Rev**. **33**, 108-22 (2004).
2. J. J. Becker and M. R. Gagné, **Acc. Chem. Res**. **37**, 798-804 (2004).
3. M. T. Reetz, **Proc. Natl. Acad. Sci. U. S. A. 101**, 5716-22 (2004).
4. B. Breit, **Angew. Chem., Int. Ed. 44**, 6816-25 (2005).
5. O. Novakova, J. Kasparkova, O. Vrana, P. M. van Vliet, J.Reedijk and V. Brabec, **Biochemistry 34**, 12369-78 (1995).
6. M. J. Bloemink, H. Engelking, S. Karentzopoulos, B. Krebs and J. Reedijk, **Inorg. Chem**. **35,** 619-27 (1996).
7. A. H. Velders, H. Kooijman, A. L. Spek, J. G. Haasnoot, D. De Vos and J. Reedijk, **Inorg. Chem**. **39**, 2966-67 (2000).
8. K. Severin, R. Bergs and W. Beck, **Angew. Chem. Int. Ed**. **37**, 1634-54 (1998).
9. R. Krämer, M. Maurus, K. Polborn, K. Sünkel, C. Robl and W. Beck, **Chem. Eur. J. 2**, 1518-25 (1996).
10. R. Fish and G. Jaouen, **Organometallics 22**, 2166-77 (2003).
11. (a) F. Joó and E. Trócsányi, **J. Organomet. Chem**. **231**, 63-72 (1982).
    (b) D.A. Laidler and D.J. Molner, **J. Organomet. Chem**. **270**, 121-29 (1984).
    (c) M. Nakagawa and H. Nakao, K. Watanabe, **Chem. Lett**. **58**, 391-400 (1985).
    (d) S. Colonna, A. Manfredi, M. Spadoni, L. Casella and M. Gullotti, **J. Chem. Soc., Perkin Trans**., 71-77 (1987).
    (e) A. Saitoh, K. Achiwa, K. Tanaka and T. Morimoto, **J. Org. Chem**. **65**, 4227-35 (2000).
12. (a) A. Mori, H. Ohno, H. Nitta, K. Tanaka and S. Inoue, **Synlett**., 563-64 (1991).
    (b) M.I. Burguete, M. Collado, J. Escorihuela, F. Galindo, E. Garcı'a-Verdugo,
    S.V. Luis and M.J. Vicent, **Tetrahedron Lett**. **44**, 6891-97 (2003).
    (c) A.V. Malkov, J.B. Hand and P. Koèovský, **Chem. Commun**. 1948-49 (2003).

13. (a) A. McClarin, L.A. Dressel and J.I. Legg, **J. Am. Chem. Soc**. **98**, 4150-54 (1976).
(b) P. Norman and D.A. Phipps, **Inorg. Chim. Acta**. **17**, L19–L20. (1976).
(c) Y. Ilan, **Inorg. Chem**. **26**, 2454-61 (1987).

14. SAINT: SAX, **Siemens Analytical Instruments Inc., Madison, WI, USA**.

15. G. Sheldrick, SADABS: **Siemens Area Detector Absorption Correction Software, University of Goettingen, Germany** (1996).

16. G. Sheldrick, SHELXL97. **Program for Structure Refinement, University of Goettingen, Germany** (1997).

17. R. Krämer, M. Maurus, R. Bergs, K. Polborn, K. Sünkel, B. Wagner and W. Beck, **Chem. Ber. 126**, 1969-76 (1993).

18. H. Brunner, T. Neuhierl and B. Nuber, , **Eur. J. Inorg. Chem.** 1877-81 (1998).

19. J.L. Farrugia, **J. Appl. Crystallogr**. **32**, 837-44 (1999).

20. (a) J.W. Faller and A.R. Lavoie, **Orgnometallics 20**, 7562-67 (2001).
(b) H.Y. Rhyoo, H.J. Park and Y.K. Chung, **Chem. Commun**. 2064-65 (2001).
(c) H.Y. Rhyoo, Y.A. Yoon, H.J. Park and Y.K. Chung, **Tetrahedron Lett. 42**, 5045-51 (2001).
(d) H.Y. Rhyoo, H.J. Park, W.H. Suh and Y.K. Chung, **Tetrahedron Lett**. **43**, 269-76 (2002).

21. (a) I.M. Pastor, P. Västilä and A. Adolfsson, **Chem. Commun**. 2046-47 (2002).
(b) I.M. Pastor, P. Västilä and A. Adolfsson, **Chem. Eur. J. 9**, 4031-40 (2003).
(c) A. Bøgevig, I.M. Pastor and A. Adolfsson, **Chem. Eur. J. 10**, 294-99 (2004).

22. (a) T. Ohta, S. Nakahara, Y. Shigemura, K. Hattori and I. Furukawa, **Chem. Lett**. **6**, 491-92 (1998).
(b) T. Ohta, S. Nakahara, Y. Shigemura, K. Hattori and I. Furukawa, **Appl. Organomet. Chem. 15**, 699-707 (2001).
(c) D.Carmona, F.J.Lahoz, R. Atencio, L.A. Oro, M.P. Lamata, F. Viguri, E.S. José, C. Vega, J. Reyes, F. Joó and A. Kathó, **Chem. Eur. J. 5**, 1544-52 (1999).
(d) A. Kathó, D. Carmona, F. Viguri, C.D. Remacha, J. Kovács, F. Joó and L.A. Oro, **J. Organomet. Chem**. **593**, 299-307 (2000).

23. (a) H. Brunner and M. Weber, M. Zabel, **Coord. Chem. Rew. 242**, 3-32 (2003).
(b) H. Brunner, M. Weber, M. Zabel and T. Zwack, **Angew. Chem. Int. Ed**. **42**, 1859-68 (2003).

24. M.A. Bennett, T.N. Huang, T.W. Manheson and A.K. Smith, **Fnorg. Synth. 21**, 74-80 (1982).