An Approach to Chiral Metal Catalysts; the Synthesis and X-Ray Crystal Structures of a Chiral Tetradentate Binaphthyl Bis-amide Ligand and its Osmium(VI)-oxo Derivative

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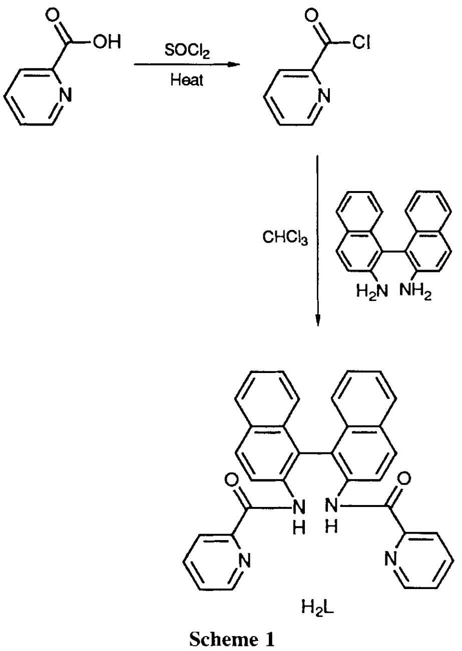
The synthesis, X-ray crystal structures and resolution of a chiral tetradentate binaphthyl bis-amide ligand and its osmium(VI)-oxo derivative are described.

Asymmetric synthesis is an important area in organic synthesis.[1] Despite the fact that impressive results have been achieved in asymmetric reduction using chiral metal catalysts, relatively few studies on asymmetric oxidation reactions have been reported.[2] The discovery that ruthenium complexes of the 2,2′-bis(diphenylphosphino)1,1′-binaphthyl[3] and aluminium complexes of 1,1′-binaphthol[4] serve as catalysts for the highly stereoselective hydrogenation and Diels–Alder reactions respectively has attracted our attention to the coordination chemistry of chelating ligands containing the binaphthyl (binap) unit. Recent research on the oxidation chemistry of osmium and manganese complexes of 1,2-bis(pyridine-2-carboxamido)benzene[5] suggest that the chiral tetradentate bina-bisamide ligand (H_2L), which should be inexpensive and easily synthesised, may find important applications in the development of chiral metal catalysts. Herein is described the preparation, resolution and X-ray crystal structures of this ligand and its osmium(VI)-oxo derivative.

The synthesis of the ligand H_2L is outlined in Scheme 1. Resolution of the pure $R(-)$, c 1.03 g/100 ml, $CHCl_3$, $\{[\alpha]_{589}^{21.5}, -11.70, [\alpha]_{546}^{21.5}, -23.06°\}$ and $S(+)$, c 0.93 g/100 ml, $CHCl_3$, $\{[\alpha]_{589}^{21.5}, +12.02, [\alpha]_{546}^{21.5}, +23.6°\}$ forms was achieved by using the optical pure $R(+)$- and $S(-)$- 2,2′-diamino-1,1′-binaphthyl[1b,6] as starting materials and by carrying out the reactions at temperatures below 5 °C. The optical purity of the ligands was ascertained using ^1H NMR spectroscopy. Fig. 1 shows the ^1H NMR spectra of the $R(-)$ and $S(+)$ forms and a racemic mixture of H_2L in $CDCl_3$ as well as in the presence of {tris [3-(heptafluoropropylhydroxymethylene)-(+)-(camphorato)europium(III)} $[Eu(hfc)_3]$. The different chemical shifts of the amido protons of the $R(-)$ and $S(+)$ forms in the presence of $[Eu(hfc)_3]$ provide a good spectroscopic handle for assuring the optical purity of ligand. As expected, the amido protons of the racemic mixture split into two signals of equal intensity in the presence of $[Eu(hfc)_3]$.



Scheme 1

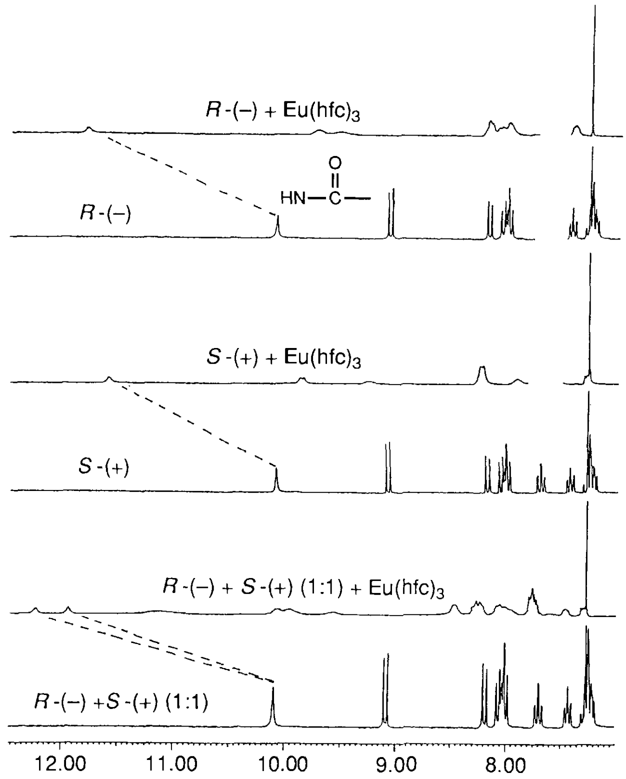


Fig. 1 ^{1}H NMR spectra of $R(-)$ and $S(+)$ forms and racemic mixture of H_2L in the absence and presence of [Eu(hfc)$_3$]

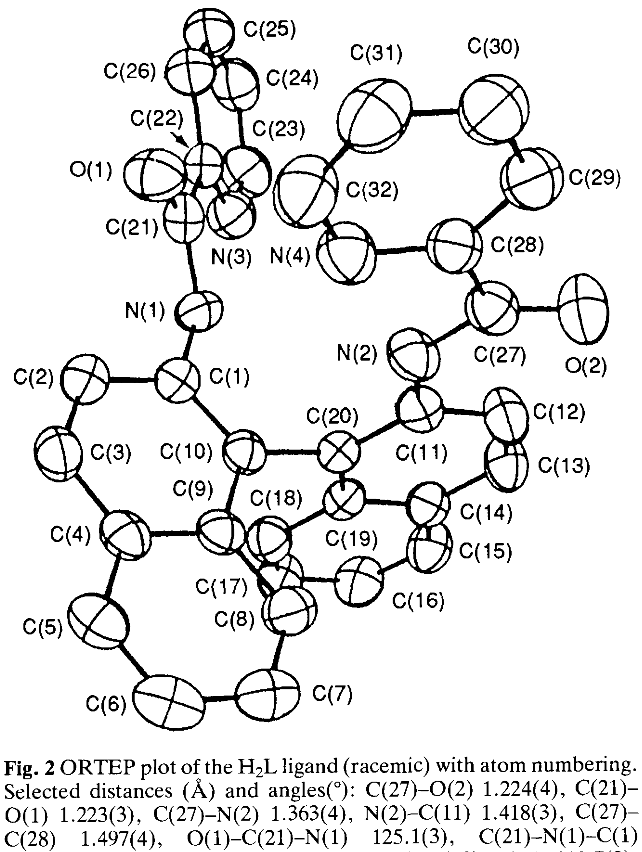


Fig. 2 ORTEP plot of the H_2L ligand (racemic) with atom numbering. Selected distances (Å) and angles(°): C(27)–O(2) 1.224(4), C(21)–O(1) 1.223(3), C(27)–N(2) 1.363(4), N(2)–C(11) 1.418(3), C(27)–C(28) 1.497(4), O(1)–C(21)–N(1) 125.1(3), C(21)–N(1)–C(1) 123.4(2), N(1)–C(1)–C(10) 118.9(2), C(10)–C(20)–C(19) 119.7(2), N(1)–C(1)–C(2) 119.8(2), C(9)–C(10)–C(20) 118.8(2).

The H_2L ligand rapidly forms complexes with transition metal ions such as Os^{VI}, Pt^{II} and Au^{III}.[7] Stirring the $R(-)$ or $S(+)$ form of H_2L (0.3 g) with $K_2[OsO_2(OH)_4]$ (0.3 g) in methanol (30 ml) at 40 °C for 1 h gave the respective R or S form of the orange product [Os^{VI}(L)(O)$_2$] in high yield (90%). The IR spectrum of the Os^{VI} complex displays an intense band at 848 cm^{-1}, which is due to the $\nu_{as}(OsO_2)$ stretch. The absence of ν(N-H) stretch at 3290–3400 cm^{-1} indicates that the coordinated amide ligand is in the deprotonated form. The structures of the racemic form of H_2L and R form of [Os^{VI}(L)(O)$_2$] have been established by X-ray crystallography.† Figs. 2 and 3 show the ORTEP plots of the ligand and the R form of [Os^{VI}(L)(O)$_2$] with atom numbering. An important structural feature of the ligand is that in its free form, the four nitrogen atoms are arranged in a distorted tetrahedral manner but become more coplanar upon coordination to osmium. This can be revealed by the dihedral angle between the planes defined by the atoms N(3), N(1), C(21)–C(26), O(1) and defined by the atomes N(2), N(4), C(27)–C(32), O(2) which is 79.39(7)° for the free ligand but 7.94(59)° for the complex. The measured dihedral angles of the two naphthalene rings of the ligand and the complex are 87.59(5) and 71.15(16)° respectively, which are higher than the value of 65.6° found in Ru[OCOC(Me)$_3$]$_2$[(S)-binap].[8] In the [Os^{VI}(L)(O)$_2$] complex, the osmium atom is six-coordinated with the two oxo groups *trans* to each other. However, the measured O(4)–Os–O(3) angle of 166.7(2)° significantly deviates from 180° which is normally expected for a *trans*-dioxometal system. The measured Os=O distances of 1.726(6) and 1.727(5) Å are in the normal range expected for *trans*-dioxoosmium(VI) complexes.[9]

The present work demonstrates a new approach to chiral multidentate chelating amide ligands having a C_2 symmetry. Given the fact that osmium(III)–amide complexes[5a] are able to catalyse alkene epoxidation by PhIO and the amount of organometallic chemistry of Os–NH$_3$ complexes,[10] it is not

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† *Crystal data*: $C_{32}H_{22}N_4O_2$ **1**, M_r = 494.55, triclinic, space group $P\bar{1}$, a = 9.540(1), b = 11.610(1), c = 12.125(1) Å, α = 112.75(1), β = 93.75(1), γ = 91.07(1)°, V = 1234.3(5) Å^3, Z = 2, D_c = 1.331 g cm^{-3}, μ(Mo-Kα) = 0.79 cm^{-1}, F(000) = 516, no. of parameters (p) 343, no. of independent data 3020, no. of observed data with $F_o > 3\sigma(F_o)(n)$ 2194, R = 0.043, R_w = 0.55. The maximum and minimum residues in the final ΔF synthesis were 0.376 and −0.220 e Å^{-3}. The structure was solved by direct methods[11] and refined by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms at calculated positions were not refined.

$OsC_{32}H_{20}N_4O_4\cdot1\frac{1}{2}[(Me)_2NCHO]\cdot3\frac{1}{2}H_2O$ **2**, M_r = 887.43, tetragonal, space group $P4_12_12$, a = 12.718(2), c = 44.781(9) Å, V = 7243(2) Å^3, Z = 8, D_c = 1.628 g cm^{-3}, D_m = 1.60 g cm^{-3}, μ(Mo-Kα) = 35.84 cm^{-1}, F(000) = 3544, no. of parameters (p) 410, no. of measured data 12 549, no. of independent data 5890, no. of observed data with $F_0 > 3\sigma(F_0)$ (n) 4944, R = 0.034, R_w = 0.041. The maximum and minimum residues in the final ΔF were 1.34 and −1.17 e Å^{-3} in the neighbourhood of the disordered solvent molecules. The osmium atom was located from a Patterson synthesis and all other non-hydrogen atoms from subsequent difference Fourier maps. Refinement was by full-matrix least-squares. All the non-hydrogen atoms in the complex were refined anisotropically and those in the solvent molecules isotropically. Hydrogen atoms in the complex were included in the structure factor calculation while those in the solvent molecules were omitted. The structures was refined with both the space group $P4_12_12$ and its enantiomorph $P4_32_12$ and the R factors were 0.034 and 0.048, respectively. Hence the space group $P4_12_12$ was confirmed and the crystal studied was of the R form.

Diffraction data for **1** and **2** were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo-Kα radiation to $2\theta_{max}$ = 44° for **1** and 47° for **2**. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied to **2** but not to **1**. All calculations were carried out on a Micro Vax II computer using the Enraf-Nonius SDP package. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1991.

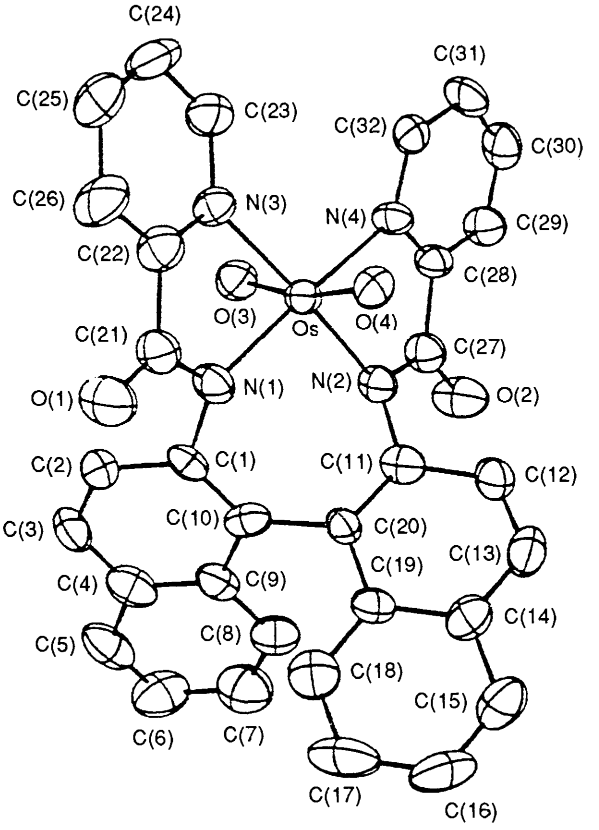

Fig. 3 ORTEP plot of the *R* form of $[Os^{VI}(L)(O)_2]$. Selected distances (Å) and angles (°): Os–O(3) 1.726(6), Os–O(4) 1.727(5), Os–N(1) 2.030(6), Os–N(2) 2.010(6), Os–N(3) 2.161(6), Os–N(4) 2.151(6), C(21)–N(1) 1.36(1), N(1)–C(1) 1.44(1), O(1)–C(21) 1.21(1), O(2)–C(27) 1.25(1), N(2)–C(27) 1.37(1), O(3)–Os–O(4) 166.6(2), N(1)–Os–N(4) 175.2(2), N(1)–Os–O(4) 94.9(2), O(2)–C(27)–N(2) 123.4(7), N(2)–C(11)–C(20) 122.4(6), Os–N(2)–C(11) 121.0(4), C(1)–C(10)–C(20) 124.5(7), C(11)–C(20)–C(10) 122.9(7).

difficult to envisage that the osmium(II) and (III) complexes of H_2L are potential catalysts for asymmetric organic transformations.

We acknowledge financial support from the University and Polytechnic Granting Committee (UPGC), the Croucher Foundation and the University of Hong Kong.

Received, 23rd November; Com. 0/05293K

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