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Synthesis and structural characterisation of new Re(III) complexes using aldimines of α-amino acids as coligands

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Abstract

Complexes of the general formula $[Re^{III}(L)Cl(PPh_3)_2]$ have been synthesised by reacting H_2L and $[ReOCl_3(PPh_3)_2]$ in ethanol. Here H_2L represents imines of α-amino acids (glycine, L-alanine, L-valine, L-phenylalanine) derived from salicylaldehyde and naphthaldehyde. The crystal structure of one complex has been determined. The complexes are mononuclear, paramagnetic and display paramagnetic ^1H NMR in $CDCl_3$ solution. Their spectral and redox properties are scrutinised.

Keywords: Rhenium(III); α-Amino acids; Schiff base

1. Introduction

Considerable attention has been given to the coordination chemistry of rhenium due to its widespread application in catalysis [1] as well as its β-emitting (Re^{186}, Re^{188}) isotopes which are used as therapeutic agents in nuclear medicine [2,3]. A sizable number of tridentate Schiff bases [4] have been used to investigate the chemistry of rhenium. However the chemistry of rhenium using aldimines of α-amino acids is not known. This has motivated us to initiate research of the chemistry of rhenium with the Schiff bases of α-amino acid.

The stability of α-amino acid Schiff base complexes depends on various factors, such as the amino acid side chain polarity [5], the metal, pH, solvent and temperature [6]. Moreover racemic complexes are also observed even in the case of optically active amino acid Schiff bases [5,7,8]. Herein we describe a successful synthesis of a hitherto unknown family of mononuclear Re(III) species chelated by aldimines of α-amino acids (glycine, L-alanine, L-valine, L-phenylalanine), starting from $[ReOCl_3(PPh_3)_2]$. The X-ray structure of one representative case is reported. Their spectral and redox behavior are discussed.

2. Experimental

2.1. Materials

All the starting chemicals were analytically pure and were used without further purification. The Schiff bases were synthesized using the reported procedure [9].

2.2. Physical measurements

UV–Vis spectra were recorded on a Perkin–Elmer LAMBDA 25 spectrophotometer. IR spectra were measured with a Perkin–Elmer L-0100 spectrophotometer. ^1H NMR and ^{31}P spectral measurements were carried out on a Bruker FT 300 MHz spectrometer with TMS as an internal reference and Bruker FT 500 MHz spectrometer, respectively. The atom-numbering scheme used for ^1H NMR is the same as that used in the crystallography and in Chart 1. Electrochemical measurements were performed (acetonitrile solution) on a CH620 electrochemical analyzer

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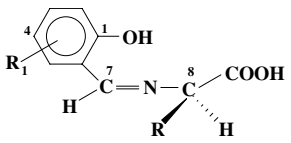

R_1 = 4,5-Benzo , R = H ; H_2L^1
R_1 = 4,5-Benzo , R = CH_3 ; H_2L^2
R_1 = 4,5-Benzo , R = CH_2Ph ; H_2L^3
R_1 = H , R = H ; H_2L^4
R_1 = H , R = CH_3 ; H_2L^5
R_1 = H , R = CH_2Ph ; H_2L^6

$[Re(L^1)Cl(PPh_3)_2]$, 1a
$[Re(L^2)Cl(PPh_3)_2]$, 1b
$[Re(L^3)Cl(PPh_3)_2]$, 1c
$[Re(L^4)Cl(PPh_3)_2]$, 2a
$[Re(L^5)Cl(PPh_3)_2]$, 2b
$[Re(L^6)Cl(PPh_3)_2]$, 2c

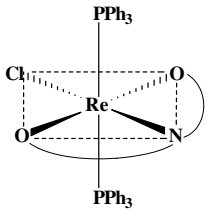

Chart 1.

using a platinum electrode under a dinitrogen atmosphere. Tetraethylammonium perchlorate (TEAP) was used as a supporting electrolyte and the potentials are referenced to the standard calomel electrode (SCE) without junction correction. Magnetic susceptibilities were measured on a PAR-155 vibrating-sample magnetometer. Microanalyses (C, H, N) were obtained from a Perkin–Elmer 2400 Series II elemental analyzer. CD spectra were recorded on a JASCO-715 polarimeter and mass spectra (70 eV) were recorded on a Qtof Micro YA263 spectrometer.

2.3. Synthesis of the complexes

The complexes $[Re^{III}(L)Cl(PPh_3)_2]$ were prepared by using a general method with $[ReOCl_3(PPh_3)_2]$ [10] as the starting material. Details are given below for one representative case (**1a**).

$[Re^{III}(L^1)Cl(PPh_3)_2]$ **1a**. 42 mg (0.18 mmol) of H_2L^1 were added to a solution of 100 mg (0.13 mmol) of $[ReOCl_3(PPh_3)_2]$ in 20 ml dry ethanol in the presence of excess PPh_3. The reaction mixture was refluxed for 6 h, producing a red precipitate. This was filtered and the solid mass was then dissolved in a minimum volume of dichloromethane and subjected to column chromatography on a silica gel column (12 × 1 cm, 60–120 mesh). A red-orange band was eluted using benzene–acetonitrile (10:1) mixture. A red-orange solid was obtained after removal of solvent from the eluate under reduced pressure. Yield: 88 mg (68%). *Anal.* Calc. for $C_{49}H_{39}NClO_3P_2Re$: C, 60.40; H, 5.04; N, 1.44. Found: C, 60.32; H, 4.98; N, 1.39%. UV–Vis (λ_{max}/nm (ε/M^{-1} cm^{-1}) CH_2Cl_2 solution): 281(20 780), 327(12 480), 365(10 695), 430(13 300), 494(4281), 1456(134). IR (KBr, cm^{-1}): ν(Re–Cl) 320; ν(C=N) 1670; $\nu(CO_2$ sym) 1310; $\nu(CO_2$ asym) 1660, 1625; ν(Re–P) 742. ^{1}H NMR ($CDCl_3$): δ 48.60 (H7, s); 9.80 (*ortho* H of PPh_3, d, J = 7.2 Hz); 8.34 (*para* H of PPh_3, t, J = 7.2 Hz); 7.87 (*meta* H of PPh_3, t, J = 7.5 Hz); −1.50 to 25.00 (ArH, 5H); −3.90 (H8, s, 2H); −23.95 (H2, d, J = 8.7 Hz). $E_{1/2}$ (Re^{III}/Re^{IV} couple): 0.33 V (ΔE_p, 80 mV); (Re^{III}/Re^{II} couple): −1.40. MS (m/z): $[M]^+$ Calcd. 973.16, 974.17, 975.17; Found: 972.89, 973.89, 974.90.

$[Re^{III}(L^2)Cl(PPh_3)_2]$ **1b**. Yield: 81 mg (62%). *Anal.* Calc. for $C_{50}H_{41}NClO_3P_2Re$: C, 60.79; H, 4.15; N, 1.41. Found: C, 60.71; H, 4.02; N, 1.38%. UV–Vis (λ_{max}/nm (ε/M^{-1} cm^{-1}) CH_2Cl_2 solution): 267(25 464), 338(11 680), 363(9585), 431(10 474), 492(3494), 1440(128). CD (λ_{max}/nm ($\Delta\varepsilon$/M^{-1} cm^{-1}) CH_2Cl_2 solution): 265(6.39), 295 (−7.65), 331(1.96), 355(−6.82), 390(1.52), 430(−19.58), 458(−10.25), 475(−10.75). IR (KBr, cm^{-1}): ν(Re–Cl) 325; ν(C=N) 1672; $\nu(CO_2$ sym) 1312; $\nu(CO_2$ asym) 1665, 1627; ν(Re–P) 747. ^{1}H NMR ($CDCl_3$): δ 47.90 (H7, s); 9.34 (*ortho* H of PPh_3, d, J = 7.8 Hz); 8.70 (*para* H of PPh_3, t, J = 7.4 Hz); 7.85 (*meta* H of PPh_3, t, J = 7.2 Hz); −1.00 to 20.00 (ArH, 5H); −5.34 (H8, d, J = 8.4 Hz); −22.22 (H2, q, J = 8.8 Hz); 1.30 (CH_3 of amino acid, d, J = 7.2 Hz, 3H). $E_{1/2}$ (Re^{III}/Re^{IV} couple): 0.44 V (ΔE_p, 80 mV); (Re^{III}/Re^{II} couple): −1.10 V. MS (m/z): $[M]^+$ Calcd. 987.46, 988.17, 985.65. Found: 987.10, 988.34, 985.70.

$[Re^{III}(L^3)Cl(PPh_3)_2]$ **1c**. Yield: 80 mg (63%). *Anal.* Calc. for $C_{56}H_{46}NClO_3P_2Re$: C, 63.19; H, 4.32; N, 1.31. Found: C, 62.89; H, 4.02; N, 1.29%. UV–Vis (λ_{max}/nm (ε/M^{-1} cm^{-1}) CH_2Cl_2 solution): 269(21 537); 332(10 752), 360(8840), 432(16 148), 489(3299), 1423(133). CD (λ_{max}/nm ($\Delta\varepsilon$/M^{-1} cm^{-1}) CH_2Cl_2): 268(10.8), 295(−14.65), 331(−3.09), 357(−9.58), 395(5.16), 427 (−22.30), 460(−17.54). IR (KBr, cm^{-1}): ν(Re–Cl) 315; ν(C=N) 1675; $\nu(CO_2$ sym) 1315; $\nu(CO_2$ asym) 1662, 1625; ν(Re–P) 748. ^{1}H NMR ($CDCl_3$): δ 49.42 (H7, s); 9.43 (*ortho* H of PPh_3, d, J = 8.4 Hz); 8.41 (*para* H of PPh_3, t, J = 8.7 Hz); 7.86 (*meta* H of PPh_3, t, J = 7.5 Hz); −1.20 to 20.00 (ArH, 10H); −5.34 (H8, d, J = 8.6 Hz); −22.25 (H2, t, J = 8.7 Hz); 0.84 (CH_2Ph, d, 2H). $E_{1/2}$ (Re^{III}/Re^{IV} couple): 0.42 V (ΔE_p, 70 mV); (Re^{III}/Re^{II} couple): −1.25 V. MS (m/z): $[M]^+$Calcd. 1063.40, 1064.20; Found: 1063.30, 1064.50.

$[Re^{III}(L^4)Cl(PPh_3)_2]$ **2a**. Yield: 78 mg (64%). *Anal.* Calc. for $C_{45}H_{35}NClO_3P_2Re$: C, 58.6; H, 3.79; N, 1.51. Found: C, 58.49; H, 3.72; N, 1.49%. UV–Vis (λ_{max}/nm (ε/M^{-1} cm^{-1}) CH_2Cl_2 solution): 275(13 585); 325(10 894), 358(8960), 410(18 067), 468(4150), 1445(125). IR (KBr, cm^{-1}): ν(Re–Cl) 332; ν(C=N) 1665; $\nu(CO_2$ sym) 1315; $\nu(CO_2$ asym) 1658, 1618; ν(Re–P) 746. ^{1}H NMR ($CDCl_3$): δ 45.50 (H7, s); 9.90 (*ortho* H of PPh_3, d, J = 7.5 Hz); 8.42 (*para* H of PPh_3, t, J = 7.3 Hz); 7.86 (*meta* H of PPh_3, t, J = 7.7 Hz); 1.00–20.00 (ArH, 3H); −8.40 (H8, s, 2H); −14.05 (H2, d, J = 7.5 Hz). $E_{1/2}$ (Re^{III}/Re^{IV} couple): 0.41 V (ΔE_p, 70 mV); (Re^{III}/Re^{II} couple): −1.15 V. MS (m/z): $[M]^+$ Calcd. 921.60, 923.20. Found: 920.80, 922.50.

$[Re^{III}(L^5)Cl(PPh_3)_2]$ **2b**. Yield: 79 mg (65%). *Anal.* Calc. for $C_{46}H_{37}NClO_3P_2Re$: C, 59.0; H, 3.95; N, 1.49. Found: C, 58.6; H, 3.88; N, 1.45%. UV–Vis (λ_{max}/nm (ε/M^{-1} cm^{-1}) CH_2Cl_2 solution): 274(20 247), 334(7457), 360

(9035), 437(13 635), 467(2742), 1453(124). CD (λ_{max}/nm ($\Delta\varepsilon$/M^{-1} cm^{-1}) CH_2Cl_2): 255(8.28), 292(−7.10), 325(0.92), 345(−4.25), 385(6.08), 415(−13.02). IR (KBr, cm^{-1}): ν(Re–Cl) 335; ν(C=N) 1669; $\nu(CO_2$ sym) 1308; $\nu(CO_2$ asym) 1661, 1618; ν(Re–P) 745. ^{1}H NMR ($CDCl_3$): δ 48.3(H7, s); 9.60 (*ortho* H of PPh_3, d, $J = 6.8$ Hz); 8.44 (*para* H of PPh_3, t, $J = 7.2$ Hz); 7.84 (*meta* H of PPh_3, t, $J = 7.5$ Hz); 1.20–20.00 (ArH, 3H); −9.80 (H8, d, $J = 8.8$ Hz); −11.85 (H2, q, $J = 7.9$ Hz), 1.42 (CH_3 of amino acid, d, $J = 6.9$ Hz, 3H). $E_{1/2}$ (Re^{III}/Re^{IV} couple): 0.42 V (ΔE_p, 80 mV); (Re^{III}/Re^{II} couple): −1.10 V. MS (*m*/*z*): $[M]^+$Calcd. 935.40, 937.80; Found: 935.60, 936.20.

$[Re^{III}(L^6)Cl(PPh_3)_2]$ **2c**. Yield: 74 mg (61%). *Anal*. Calc. for $C_{51}H_{42}NClO_3P_2Re$: C, 60.5; H, 4.15; N, 1.38. Found: C, 60.32; H, 4.08; N, 1.36%. UV–Vis (λ_{max}/nm (ε/M^{-1} cm^{-1}) CH_2Cl_2 solution): 271(18 575), 337(11 220), 365(9670), 439(10 230), 474(3982), 1437(132). CD (λ_{max}/nm ($\Delta\varepsilon$/M^{-1} cm^{-1}) CH_2Cl_2): 265(6.80), 295(−7.42), 322(0.62), 346(−6.49), 380(6.18), 418(−10.52). IR (KBr, cm^{-1}): ν(Re–Cl) 327; ν(C=N) 1676; $\nu(CO_2$ sym) 1316; $\nu(CO_2$ asym) 1659, 1622; ν(Re–P) 746. ^{1}H NMR ($CDCl_3$): δ 49.80 (H7, s); 9.50 (*ortho* H of PPh_3, d, $J = 6.6$ Hz); 8.42 (*para* H of PPh_3, t, $J = 7.2$ Hz); 7.84 (*meta* H of PPh_3, d, $J = 7.5$ Hz); 1.20–20.00 (ArH, 8H); −9.60 (H8, d, $J = 8.5$ Hz); −12.30 (H2, t, $J = 7.8$ Hz); 0.88 (CH_2Ph, d, 2H). $E_{1/2}$(Re^{III}/Re^{IV} couple): 0.45 V (ΔE_p, 80 mV); (Re^{III}/Re^{II} couple): −1.30 V. MS (*m*/*z*): $[M]^+$Calcd. 1011.80, 1009.30; Found: 1010.60, 1008.90.

2.4. X-ray structure determination

X-ray quality single crystals for the complex $[Re^{III}(L^1)Cl(PPh_3)_2]$ were grown by slow diffusion of diethyl ether into a dichloromethane solution. The X-ray intensity data were measured at 293 K on a Bruker AXS SMART APEX CCD diffractometer (Mo Kα, $\lambda = 0.71073$ Å). The detector was placed at a distance of 6.03 cm from the crystal. A total of 606 frames were collected with a scan width of 0.3° with different settings of φ. The data were reduced in SAINTPLUS [11] and an empirical absorption correction was applied using the SADABS package [12]. The metal atom was located by direct methods using SIR92 [12]. The structure was refined by the full matrix least-square method using SHELXL97 [13], that was present in the program suite WINGX (Version 1.63.04a) [14]. All non-hydrogen atoms were refined anisotropically. The azomethine hydrogen atom was directly located in difference Fourier maps and the remaining hydrogen atoms were included in calculated positions. Significant crystal data are given in Table 1.

Table 1
Crystal data and structural refinement parameters for $[Re^{III}(L^1)Cl(PPh_3)_2]\cdot CH_2Cl_2\cdot H_2O$

	$[Re^{III}(L^1)Cl(PPh_3)_2].CH_2Cl_2\cdot H_2O$
Formula	$C_{50}H_{41}Cl_2O_{0.5}NO_4P_2Re$
Formula weight	1056.60
Crystal system	orthorhombic
Space group	*F2dd*
a (Å)	17.444(3)
b (Å)	32.079(6)
c (Å)	33.483(6)
V (Å^3)	18 737(5)
Z	16
D_{calc} (Mg m^{-3})	1.498
μ (mm^{-1})	2.849
θ (°)	1.76–27.49
Measured reflections	36 191
Unique refection (R_{int})	9472 (0.0290)
Temperature (K)	293(2)
R_1,[a] wR_2[b] [$I > 2\sigma(I)$]	0.0306, 0.0719
Goodness-of-Fit on F^2	1.060

[a] $R_1 = \sum|F_o| - |F_c|/\sum|F_o|$.
[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

3. Result and discussion

3.1. Synthesis

Aldimines of four α-amino acids (glycine, L-alanine, L-valine and L-phenylalanine) have been used in the present work. The aldimine ligands will be abbreviated as H_2L (Chart 1), the two H atoms (phenolic and carboxylic) being potentially dissociable. The abbreviations for specific Schiff bases are given in Chart 1.

The stoichiometric reaction of $[ReOCl_3(PPh_3)_2]$ with the appropriate ligand in boiling ethanol afforded orange-red coloured complexes of the general formula $[Re^{III}(L)Cl(PPh_3)_2]$. It is noted that when the reaction is carried out in the presence of excess PPh_3 there is an increase in yield of $[Re^{III}(L)Cl(PPh_3)_2]$. This observation indicates that the reduction from Re(V) to Re(III) takes place via the abstraction of the Re=O oxygen atom by PPh_3 [4e].

The characterization data of the complexes are given in the Section 2. A strong C=N stretch is observed at ~1670 cm^{-1}. Carboxylate monocoordination [15,16] is consistent with the presence of one symmetric (~1310 cm^{-1}) and two asymmetric (~1620 and 1660 cm^{-1}) stretches. The Re–Cl and Re–P stretches occur at ~325 and ~745 cm^{-1} respectively.

Electro spray ionization mass spectrometry (ESI-MS) of compound **1a** displayed the highest *m*/*z* peak at 972.90, unambiguously assigned to the $[Re^{III}(L^1)Cl(PPh_3)_2]$ parent ion on the basis of the isotopic distribution of ^{35,37}Cl and ^{185,187}Re. The pattern for $(M–H)^+$ is also observed.

3.2. Crystal structure

The crystal structure of $[Re^{III}(L^1)Cl(PPh_3)_2]$ has been determined. The molecular view is shown in Fig. 1 and selected bond parameters are given in Table 2.

The tridentate meridionally disposed $[L^1]^{2-}$ contains two excellently planar segments ($OC_{10}H_6CHN$ and CCO_2; mean deviation <0.02 Å) and the dihedral angle between them is 5.8 Å. In the distorted ReO_2NClP_2 octahedral environment two oxygen atoms, one chlorine atom

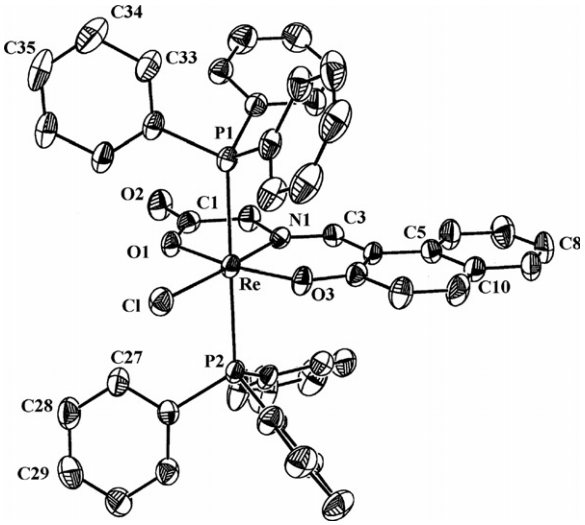

Fig. 1. Perspective view and atom-labelling scheme for the molecule $[Re^{III}(L^1)Cl(PPh_3)_2]$. All non-hydrogen atoms are represented by their 30% thermal probability ellipsoids.

and one nitrogen atom lie in the equatorial plane, whereas the axial positions are occupied by two phosphine ligands. The two Re–O bond distances are not similar and span the range 1.89–1.98 Å. The Re–P bond distances are slightly larger than for previously reported rhenium(III) mixed ligand phosphine Schiff base complexes [17]. The Re–Cl and Re–N bond distances are usual [18] (Table 2).

3.3. Electrochemical studies

The redox properties of the Re(III) α-amino acid Schiff base complexes have been examined by cyclic voltammetry using platinum as the working electrode and SCE as the reference electrode. The cyclic voltammogram was recorded at a scan rate of 50 mV/s. The relevant data are given in Section 2 and a representative voltammogram is shown in Fig. 2.

All the complexes exhibit one quasi-reversible and one irreversible one-electron wave in acetonitrile solution.

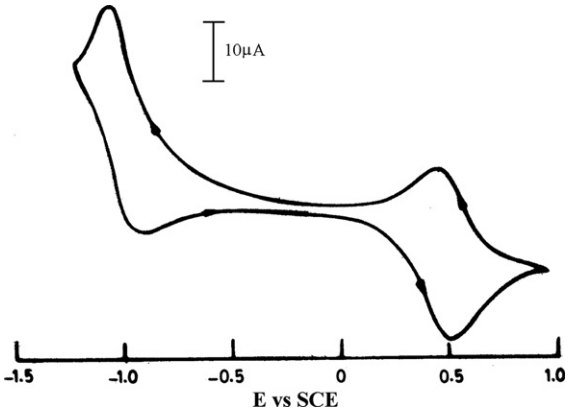

Fig. 2. Cyclic voltammogram of ca. 10^{-3} M solution of $[Re^{III}(L^2)Cl(PPh_3)_2]$ in acetonitrile.

The anodic signal (~0.50 V) at a more positive potential is assigned to the oxidation couple $Re^{IV/III}$ while the couple at ~−1.10 V is believed to be the $Re^{III/II}$ reduction. This redox behavior is consistent with previously known Re(III) complexes [17,19,20].

3.4. Magnetism and NMR spectra

The complexes show a magnetic moment value of ~1.94 BM, corresponding to mononuclear octahedral rhenium(III) d^4 species. The low value of the magnetic moment can be attributed to the large spin–orbit coupling of the rhenium(III) ion [21,22]. The complexes display well-resolved paramagnetic ^1H NMR resonances in $CDCl_3$ solution and the chemical shifts are observed within the range ~−25.00 to +50.00 ppm. The resonances are assigned on the basis of spin–spin structure and spin intensity of the respective rhenium(III) complexes.

In the present case, the absence of phosphorous-proton coupling is probably due to a rapid relaxation of the phosphorous nuclei through an electron-nuclear mechanism to the paramagnetic Re(III) center [23–28]. The paramagnetically shifted ^1H NMR spectrum of a representative case is shown in Fig. 3 and the chemical shift values of the

Table 2
Selected structural parameters for $[Re^{III}(L^1)Cl(PPh_3)_2]$ (distances in Å and angles in °)

Distances			
Re(1)–O(1)	1.896(3)	Re(1)–P(1)	2.5769(12)
Re(1)–O(2)	1.980(3)	Re (1)–P(2)	2.5807(12)
Re(1)–N(1)	2.013(4)	Re(1)–Cl(1)	2.4101(14)
Angles			
O(1)–Re(1)–O(2)	168.07(12)	O(2)–Re(1)–P(2)	92.24(10)
O(1)–Re(1)–N(1)	88.80(14)	N(1)–Re(1)–P(2)	91.54(12)
O(2)–Re(1)–N(1)	79.38(15)	N(1)–Re(1)–P(1)	91.60(12)
O(1)–Re(1)–Cl(1)	94.64(10)	N(1)–Re(1)–Cl(1)	176.56(12)
O(2)–Re(1)–Cl(1)	97.18(11)	Cl(1)–Re(1)–P(1)	88.40(5)
O(1)–Re(1)–P(1)	87.58(12)	Cl(1)–Re(1)–P(2)	88.65(5)
O(2)–Re(1)–P(1)	91.17(10)	P(1)–Re(1)–P(2)	175.74(5)
O(1)–Re(1)–P(2)	89.60(12)		

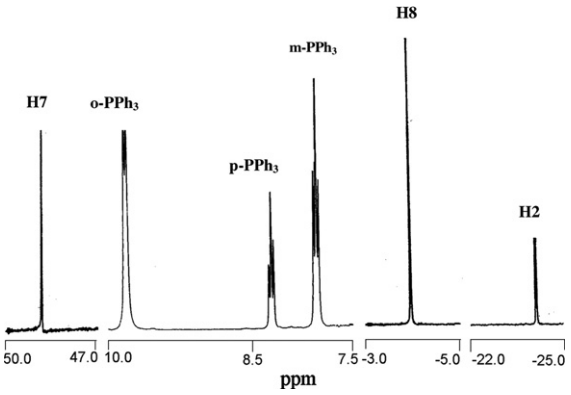

Fig. 3. ^1H NMR spectrum of $[Re^{III}(L^1)Cl(PPh_3)_2]$ in $CDCl_3$ at room temperature.

complexes are given in Section 2. The numbering scheme is as in Chart 1 and Fig. 1. In solution, the azomethine hydrogen occurs as a singlet at ~49.00 ppm. The ortho protons of the coordinated phosphine appear as a doublet at ~9.50 ppm ($J = 7$–8 Hz). The meta and para protons are observed as triplets at ~7.80 and 8.40 ppm respectively, with a coupling constant $J = 7$–9 Hz. All other aromatic H-atoms fall in the range +25.00 to −25.00 ppm. The α-hydrogen atom of the amino acid residue appears as singlet/multiplet in the negative region.

The ^{31}P NMR signals for the phosphines coordinated to the Re(III) center were not observed and the result is consistent with previously reported paramagnetic Re(III) complexes [26,29,30].

3.5. Electronic and CD spectra

The electronic and CD spectra were recorded in dichloromethane solution. The electronic and CD spectral data are given in Section 2. The CD spectra of the Re(III) chelates of amino acid Schiff bases below 550 nm are given in Fig. 4.

The low energy d–d absorption of the complexes is found near 1000 and 1470 nm. A moderately intense absorption band is observed at ~360 nm and this can be attributed to the π–π* transition originating mainly from the azomethine chromophore. The bathochromic shift of this band compared to the free amino acid Schiff bases [31]is due to the increase of conjugation in the molecule upon coordination. The intense absorption band at higher energy, ~270 nm, is presumably from the π–π* transition of the benzene/naphthalene ring of the Schiff bases. The CD spectra are more informative than the corresponding absorption spectra. A careful comparison of the CD spectra of the Re(III) amino acid Schiff base complexes reveal that the sign and pattern of three bands or shoulder in the UV region as well as the Cotton effect is same within the entire family. This observation clearly indicates that the coordinating ligands adopt a common conformation. It has been recognized that a negative azomethine CD band corresponds to the L-absolute configuration of the amino acid residue. The present results are consistent with previously reported complexes using aldimines of α-amino acids [6,32].

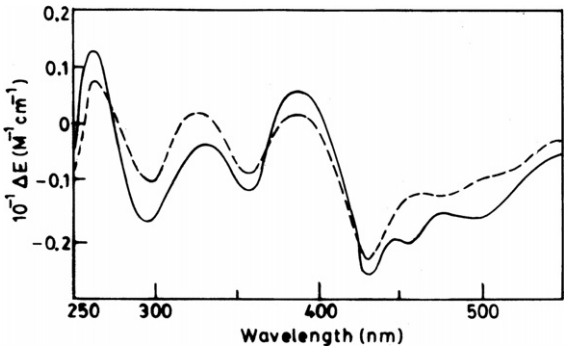

Fig. 4. Circular dichroism spectra of **1b** (——) and **1c** (—) in dry dichloromethane solution.

4. Conclusion

The Schiff bases of salicyladehyde/naphthaldehyde and α-amino acids (glycine, L-alanine, L-valine, L-phenylalanine) react with $[ReOCl_3(PPh_3)_2]$ toafford Re(III) complexes of the general formula $[Re^{III}(L)Cl(PPh_3)_2]$. The species $[Re^{III}(L)Cl(PPh_3)_2]$ represent the first example of structurally characterized Re(III) complexes incorporating α-amino acid Schiff bases as a coligand. The CD spectra confirm the L-absolute configuration of the amino acids in the complexes. Our search for new rhenium complexes of Schiff bases of different amino acids and peptides are in progress.

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Appendix A. Supplementary material

CCDC 285571 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.03.036.

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