Novel oxorhenium(V) '3+1' mixed ligand complexes with 3-thiapentane-1,5-dithiolate and functional mercaptobenzoyl amino acid ethyl ester

ARTICLE *in* INORGANICA CHIMICA ACTA · JUNE 2007

Impact Factor: 2.05 · DOI: 10.1016/j.ica.2007.06.038

4 AUTHORS, INCLUDING:

Shubhamoy Chowdhury
Tripura University
41 PUBLICATIONS **328** CITATIONS
SEE PROFILE

Ali Canlier
Korea Advanced Institute of Science and Te…
15 PUBLICATIONS **153** CITATIONS
SEE PROFILE

Available online at www.sciencedirect.com
ScienceDirect
Inorganica Chimica Acta 361 (2008) 145–152
Inorganica Chimica Acta
www.elsevier.com/locate/ica

Novel oxorhenium(V) '3+1' mixed ligand complexes with 3-thiapentane-1,5-dithiolate and functional mercaptobenzoyl amino acid ethyl ester

Shubhamoy Chowdhury, Ali Canlier, Nobuyoshi Koshino, Yasuhisa Ikeda *

Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, 2-12-1-N1-34 O-okayama, Meguro-ku, Tokyo 152-8550, Japan

Received 24 April 2007; received in revised form 19 June 2007; accepted 23 June 2007
Available online 1 July 2007

Abstract

Oxorhenium(V) complexes with '3+1' mixed ligands, [ReO(SSS)L], where SSS is η^3-($SCH_2CH_2SCH_2CH_2S$), L = η^1-(C_6H_4COOH-4-S), η^1-($C_6H_4CONHCH_2COOEt$-4-S), η^1-($C_6H_4CONHCH(CH_3)COOEt$-4-S), and η^1-($C_6H_4CONHCH(CH_2Ph)COOEt$-4-S), have been synthesized. These L ligands and [ReO(SSS)L] complexes were characterized by IR, ^{1}H NMR, ^{13}C NMR, and MAS spectrometers. Molecular structure of [ReO(SSS){η^1-(C_6H_4COOH-4-S)}] complex was determined to be a distorted square pyramidal by single crystal X-ray analytical method.

Keywords: Oxorhenium(V) complexes; Molecular structure; Amino acid esters; '3+1' mixed ligands; Thiolate

1. Introduction

Oxorhenium(V) complexes as radiopharmaceuticals for therapy and diagnosis have been paid attention, because of their suitable radionuclear properties, i.e., ^{186}Re: E_{max} = 1.1 MeV for β-emission and E_{max} = 0.137 MeV for γ-emission with $t_{1/2}$ = 90.6 h, ^{188}Re: E_{max} = 2.1 MeV for β-emission and E_{max} = 0.155 MeV for γ-emission with $t_{1/2}$ = 17 h [1].

Generally, integrated and bifunctional approaches have been used for drug designing of Re compounds [2,3]. In such ways, '3+1' mixed ligand approach has been proposed for developing novel radiopharmaceuticals containing oxo-Re(V), in which ReO^{3+} core is coordinated by tridentate dithiolates (SXS, X = O, S, or NR) and unidentate thiolates. This approach has been paid much attention [4–15], because the oxo-Re(V) complexes with '3+1' mixed ligands enable the coupling of biologically relevant groups and molecules, and hence are expected to generate radiopharmaceuticals with various functions, e.g., the inhibitors of protease such as cathepsin, the receptors in the central nervous system (CNS), the agents for the assessment of brain perfusion, the application in nuclear medicine oncology, and so on [16–26].

However, it has been reported that the oxo-Re(V) complexes with '3+1' mixed ligands are unstable in vitro and in vivo due to the metabolism and replacement of the unidentate ligands by thiolated nucleophiles such as glutathione [27–29]. Hence, the oxo-Re(V) complexes with mixed ligands for overcoming such problems have been synthesized and characterized [30–35].

On the other hand, the introduction of the pendent ester groups (PEGs) on the unidentate thiolate coligand has been undertaken to develop new oxo-Re(V) complexes for the metabolic pathway in brain cells, because hydrolysis of PEGs by intracerebral esterases is expected to provoke trapping of oxo-Re(V) with PEGs in brain tissue due to their transformation to hydrophilic and non-diffusible metabolites [36,37].

* Corresponding author. Fax: +81 3 5734 3061.
E-mail address: yikeda@nr.titech.ac.jp (Y. Ikeda).

0020-1693/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2007.06.038

On the basis of the background mentioned above, we synthesized [ReO(SSS)L] complexes, where SSS is η^3-($SCH_2CH_2SCH_2CH_2S$), L = η^1-(C_6H_4COOH-4-S), η^1-($C_6H_4CONHCH_2COOEt$-4-S), η^1-($C_6H_4CONHCH(CH_3)$-COOEt-4-S), and η^1-($C_6H_4CONHCH(CH_2Ph)COOEt$-4-S). In the syntheses of these complexes, we used a bifunctional approach. The oxo-Re(V) moiety is linked to the amino acid residues through a *p*-benzoyl group. These complexes were characterized by IR, ^{1}H NMR, ^{13}C NMR, and electrospray ionization mass (ESIM) spectrometers. In addition, the single crystal X-ray analysis of [ReO(SSS){η^1-(C_6H_4COOH-4-S)}] complex was carried out to examine the basic structure of [ReO(SSS)L].

2. Experimental

2.1. Materials and methods

All chemicals were purchased from Sigma/Aldrich and used as received. Solvents were purified prior to use. Dichloromethane-d_2 and tetrahydrofuran-d_8 (Acrose Organics, 99.5 atom % D) were used as NMR lock reagents.

Infrared and UV–Vis spectra were recorded on Shimadzu FTIR-8100 and Shimadzu UV-3150 spectrophotometers, respectively. Elemental analyses for C, H, and N were conducted using a Perkin–Elmer 2400/II automatic elemental analyzer. ^{1}H and ^{13}C NMR spectra were measured at 300.4 MHz and 30.35 MHz on a JEOL JNM-LA300WB spectrometer, respectively. Chemical shifts for ^{1}H and ^{13}C NMR were recorded by using $(CH_3)_4Si$ as an internal standard.

Electrospray ionization mass (ESIM) spectra were recorded on a Qtof Micro YA263 spectrometer.

2.2. Synthetic procedure for p-tritylmercaptobenzoic acid (*2*)

p-Mercaptobenzoic acid (**1**) (3.084 g, 20 mmol) and trityl chloride (5.575 g, 20 mmol) were dissolved in 50 cm^3 of *N*,*N*-dimethylformamide (DMF). After stirring the reaction mixture at an ambient temperature for 36 h, the solvent was removed in vacuum. Resulting white residue was dissolved in 200 cm^3 of chloroform and washed with distilled water (50 cm^3 × 3). The solution was dried over $MgSO_4$ and a white pure solid was obtained after evaporating under reduced pressure (6.4 g, 81%). *Anal.* Calc. for $C_{26}H_{20}O_2S$: C, 78.74; H, 5.09. Found: C, 78.18; H, 5.28%. IR (KBr, cm^{-1}) 1684 (vs, acid C=O). UV–Vis (CH_2Cl_2, λ/nm, (ε/dm^3 mol^{-1} cm^{-1})): 305 (6930). ^{1}H NMR (CD_2Cl_2, ppm): 7.58 (2H, d, J = 8.7 Hz, ArH); 7.34–7.14 (15H, m, PhH); 7.94 (2H, d, J = 8.7 Hz, ArH). ^{13}C NMR (CD_2Cl_2, ppm): 174.1, 145.6, 138.3, 137.8, 133.8, 130.9, 129.8, 128.4, 127.5, 71.5. Mass spectrum: requires for $C_{26}H_{20}O_2SNa$ 419, found $[M+Na]^+$ 419.

2.3. General synthetic procedure for N-p-tritylmercaptobenzoyl amino acid esters

Amino acid ethyl ester (4 mmol) and triethylamine (Et_3N) (1.0 cm^3) were added to dichloromethane (60 cm^3) solution containing *p*-tritylmercaptobenzoic acid (**2**) (1.190 g, 3 mmol), 1-hydroxy-benzotriazole (HOBt) (0.540 g, 4 mmol), and 1,3-dicyclohexylcarbodiimide (DCC) (0.825 g, 4 mmol) at 0 °C. After 30 min, the solution was warmed to room temperature and allowed to keep for 48 h. The precipitated *N*,*N*-dicyclohexylurea was removed by filtration and the filtrate was washed with aqueous solution of 10% sodium hydrogen carbonate and 5% citric acid. The resulting solution was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure to obtain a white solid.

2.3.1. N-p-Tritylmercaptobenzoyl glycine ethyl ester (*3a*)

Glycine ethyl ester hydrochloride (0.560 g, 4 mmol) was used as the amino acid ethyl ester. Recrystallization was performed by using a mixture of dichloromethane and methanol. The title compound **3a** was obtained as a white solid (yield 0.840 g, 58%). *Anal.* Calc. for $C_{30}H_{27}NO_3S$: C, 74.81; H, 5.66; N, 2.91. Found: C, 75.05; H, 5.72; N, 2.63%. IR (KBr, cm^{-1}): 1755 (vs, ester C=O), 1640 (vs, amide C=O). UV–Vis (CH_2Cl_2, λ/nm, (ε/dm^3 mol^{-1} cm^{-1})): 294 (9654). ^{1}H NMR (CD_2Cl_2, ppm): 7.43–7.19 (17H, m, 2ArH and 15 PhH); 7.02 (2H, d, J = 8.3 Hz, ArH); 6.50 (1H, br s, –N*H*–); 4.22 (2H, q, J = 7.2 Hz, –OC*H*$_2$–CH$_3$); 4.12 (2H, d, J = 5.4 Hz, –NH–C*H*2–CO–); 1.27 (3H, t, J = 7.2 Hz, –O–CH$_2$C*H*$_3$). ^{13}C NMR (CD_2Cl_2, ppm): 170.4, 167.2, 144.7, 140.6, 133.0, 132.6, 130.5, 128.4, 127.5, 127.1, 71.6, 62.1, 42.3, 14.5. Mass spectrum requires for $C_{30}H_{27}NO_3SNa$ 504, found $[M+Na]^+$ 504.

2.3.2. N-p-Tritylmercaptobenzoyl-L-alanine ethyl ester (*3b*)

L-Alanine ethyl ester hydrochloride (0.600 g, 3.9 mmol) was used as the amino acid ethyl ester. Recrystallization from the mixture of dichloromethane and diethyl ether gave the title compound **3b** as a white solid (yield 0.750 g, 52%). *Anal.* Calc. for $C_{31}H_{29}NO_3S$: C, 75.12; H, 5.90; N, 2.83. Found: C, 75.38; H, 6.10; N, 2.69%. IR (KBr, cm^{-1}): 1743 (vs, ester C=O), 1647 (vs, amide C=O); UV–Vis (CH_2Cl_2, λ/nm, (ε/dm^3 mol^{-1} cm^{-1})): 295 (10850). ^{1}H NMR (CD_2Cl_2, ppm): 7.34–7.10 (17H, m, 2ArH and 15PhH); 6.92 (2H, d, J = 8.4 Hz, ArH); 6.50 (1H, d, J = 7.2 Hz, –N*H*–); 4.56 (1H, m, –C*H*–CH$_3$) 4.10 (2H, q, J = 7.0 Hz, –OC*H*$_2$–CH$_3$); 1.35 (3H, d, J = 7.2 Hz, –CH–C*H*$_3$); 1.18 (3H, t, J = 7.2 Hz, –O–CH$_2$C*H*$_3$). ^{13}C NMR (CD_2Cl_2, ppm): 173.5, 166.4, 144.7, 140.6, 133.0, 132.6, 130.5, 128.4, 127.5, 127.1, 71.6, 62.1, 49.2, 18.8, 14.4. Mass spectrum requires for $C_{31}H_{29}NO_3SNa$ 518, found $[M+Na]^+$ 518.

*2.3.3. N-p-Tritylmercaptobenzoyl-L-phenylalanine ethyl ester (**3c**)*

L-Phenylalanine ethyl ester hydrochloride (0.920 g, 4 mmol) was used as the amino acid ethyl ester. Recrystallization from the mixture of dichloromethane and methanol gave the title compound **3c** as a white solid (yield 1.062 g, 62%). *Anal.* Calc. for $C_{37}H_{33}NO_3S$: C, 77.72; H, 5.82; N, 2.45. Found: C, 77.34; H, 5.65; N, 2.62%. IR (KBr, cm^{-1}): 1739 (vs, ester C=O), 1637 (vs, amide C=O); UV–Vis (CH_2Cl_2, λ/nm, (ε/$dm^3\,mol^{-1}\,cm^{-1}$)): 295 (13 350). ^1H NMR (CD_2Cl_2, ppm): 7.33–7.02 (17H, m, 2ArH and 15PhH); 6.89 (2H, d, $J = 8.4$ Hz, 2ArH); 6.33 (2H, d, $J = 7.5$ Hz, –N*H*–CH–); 4.83 (1H, td, $J_t = 6$ $J_d = 4.2$ Hz, –NH–C*H*–) 4.08 (2H, q, $J = 6.9$ Hz, –O$CH_2$$CH_3$); 3.09 (2H, ddd, $J = 5$ and 6 Hz, –CHCH_2Ph) 1.16 (3H, t, $J = 7.2$ Hz, –OCHCH_3). ^{13}C NMR (CD_2Cl_2, ppm): 172.0, 166.4, 144.7, 140.6, 136.7, 132.9, 132.8, 130.5, 129.9, 129.0, 128.4, 127.5, 127.0, 71.5, 62.2, 38.4, 14.5. Mass spectrum requires for $C_{37}H_{33}NO_3SNa$ 594, found $[M+Na]^+$ 594.

2.4. General synthetic procedure for thiol deprotection from N-p-tritylmercaptobenzoyl amino acid ethyl esters

N-p-Tritylmercaptobenzoyl amino acid ethyl esters (**3a**, **3b**, or **3c**) were dissolved in a mixture of trifluoroacetic acid (TFA) (2 cm^3) and triethylsilane (TES) (2 cm^3). After stirring the mixture for 2 h, solvent was removed under a stream of nitrogen to obtain a sticky white solid mass. The white solid mass was washed vigorously with *n*-hexane.

*2.4.1. N-p-Mercaptobenzoyl glycine ethyl ester (**4a**)*

N-p-Tritylmercaptobenzoyl glycine ethyl ester (**3a)** (0.725 g, 1.5 mmol) was used as the amino acid ethyl ester. Recrystallization from the mixture of dichloromethane and *n*-hexane gave the title compound **4a** as a white solid (yield 0.235 g, 65%). *Anal.* Calc. for $C_{11}H_{13}NO_3S$: C, 55.20; H, 5.48; N, 5.62. Found: C, 54.94; H, 5.76; N, 5.62%. IR (KBr, cm^{-1}): 2558 (s, S–H); 1740 (vs, ester C=O), 1645 (vs, amide C=O); UV–Vis (CH_2Cl_2, λ/nm, (ε/$dm^3\,mol^{-1}\,cm^{-1}$)): 268 (3620). ^1H NMR (CD_2Cl_2, ppm): 7.66 (2H, d, $J = 8.4$ Hz, ArH); 7.33 (2H, d, $J = 8.1$ Hz, ArH); 6.86 (1H, br s, –N*H*–); 4.27–4.17 (4H, m, –NH–CH_2 and –O$CH_2$$CH_3$) 3.73 (1H, s, –S*H*); 1.29 (3H, t, $J = 7.2$ Hz, –OCH$_2$CH_3). ^{13}C NMR (CD_2Cl_2, ppm): 170.3, 168.3, 138.1, 130.5, 129.0, 128.4, 62.4, 42.6, 14.5. Mass spectrum requires for $C_{11}H_{13}NO_3SNa$ 262, found $[M+Na]^+$ 262.

*2.4.2. N-p-Mercaptobenzoyl-L-alanine ethyl ester (**4b**)*

N-p-Tritylmercaptobenzoyl-L-alanine ethyl ester (**3b**) (0.695 g, 1.4 mmol) was used as the amino acid ethyl ester. Recrystallization was performed using the mixture of acetone and *n*-hexane. The title compound **4b** was obtained as a white solid (yield 0.220 g, 62%). *Anal.* Calc. for $C_{12}H_{15}NO_3S$: C, 56.89; H, 5.97; N, 5.53. Found: C, 57.08; H, 5.73; N, 5.68%. IR (KBr, cm^{-1}): 2557 (s, S–H); 1737 (vs, ester C=O), 1641 (vs, amide C=O); UV–Vis (CH_2Cl_2, λ/nm, (ε/$dm^3\,mol^{-1}\,cm^{-1}$)): 268 (3810). ^1H NMR (CD_2Cl_2, ppm): 7.65 (2H, d, $J = 8.7$ Hz, ArH); 7.33 (2H, d, $J = 8.4$ Hz, ArH); 6.80 (1H, br s, –N*H*–); 4.70 (1H, m, –NHC*H*); 4.22 (2H, q, $J = 7.2$ Hz, –O$CH_2$$CH_3$); 3.71 (1H, s, –S*H*): 1.50 (3H, d, –CHCH_3) 1.29 (3H, t, $J = 7.2$ Hz, –OCH$_2$CH_3). ^{13}C NMR (CD_2Cl_2, ppm): 171.4, 168.9, 129.1, 128.4, 127.3, 62.3, 49.4, 18.82, 14.5. Mass spectrum requires for $C_{12}H_{15}NO_3SNa$ 276, found $[M+Na]^+$ 276.

*2.4.3. N-p-Mercaptobenzoyl-L-phenylalanine ethyl ester (**4c**)*

N-p-Tritylmercaptobenzoyl-L-phenylalanine ethyl ester (**3c**) (1.145 g, 2 mmol) was used as the amino acid ethyl ester. Recrystallization from the mixture of dichloromethane and *n*-hexane gave the title compound **4c** as a white solid (yield 0.365 g, 55%). *Anal.* Calc. for $C_{18}H_{19}NO_3S$: C, 65.62; H, 5.82; N, 4.25. Found: C, 65.35; H, 5.98; N, 4.32%. IR (KBr, cm^{-1}): 2557 (s, S–H); 1729 (vs, ester C=O); 1640 (vs, amide C=O); UV–Vis (CH_2Cl_2, λ/nm, (ε/$dm^3\,mol^{-1}\,cm^{-1}$)): 265 (18 080). ^1H NMR (CD_2Cl_2, ppm): 7.57 (2H, d, $J = 8.4$ Hz, ArH); 7.31–7.13 (5H, m, Ph); 7.15 (2H, d, $J = 7.8$ Hz, ArH); 6.50 (1H, d, $J = 6.6$ Hz, –N*H*); 4.97 (1H, m, –NHC*H*); 4.18 (2H, q, $J = 7.2$ Hz, –O$CH_2$$CH_3$); 3.68 (1H, s, –S*H*): 3.22 (2H, m, –CHCH_2Ph); 1.26 (3H, t, $J = 7.2$ Hz, –OCH$_2$CH_3). ^{13}C NMR (CD_2Cl_2, ppm): 172.1, 166.4, 137.2, 136.8, 131.6, 130.0, 129.1, 128.9, 128.2, 127.6, 62.2, 54.7, 38.4, 14.4. Mass spectrum requires for $C_{18}H_{19}NO_3SNa$ 352, found $[M+Na]^+$ 352.

2.5. General procedure for synthesizing '3+1' oxorhenium(V) complexes from [ReO{η^3-($SCH_2CH_2SCH_2CH_2S$)}Cl]

To dichloromethane solution (20 cm^3) containing [ReO{η^3-($SCH_2CH_2SCH_2CH_2S$)}Cl] (abbreviated as [ReO(SSS)Cl]) (0.098 g, 0.25 mmol) was added dropwise a solution of 1 equiv. (0.25 mmol) of monothiol. When Et_3N (0.14 cm^3, 1.0 mmol) was added to the mixture, the color of the solution was immediately changed from blue to red. The solution was stirred for an additional 2 h. The red dichloromethane solution was washed with water (3 × 25 cm^3) and dehydrated by adding anhydrous $MgSO_4$. Slow evaporation of the solvents at ambient temperature gave the red solid as product.

*2.5.1. [ReO{η^3-($SCH_2CH_2SCH_2CH_2S$)}{η^1-(C_6H_4COOH-4-S)}] (**5**)*

The *p*-mercaptobenzoic acid (**1**) was used as the monothiol. In this case, the red precipitates immediately appeared with the addition of **1** to the dichloromethane solution of [ReO(SSS)Cl]. The precipitates were filtered off, washed with water, and dried under vacuum over silica gel. Recrystallization from the mixture of DMF and diethyl ether gave the title compound. Single crystals of

complex **5** were grown by slowly evaporating tetrahydrofuran (THF) solution of **5** at ambient temperature (yield: 0.083 g, 65%). *Anal.* Calc. for $C_{11}H_{13}O_3ReS_4$: C, 26.02; H, 2.58. Found: C, 25.88; H, 2.70%. IR (KBr, cm^{-1}) 1694 (vs, acid C=O); 967 (vs, Re=O); UV–Vis (DMF, λ/nm, (ε/$dm^3\,mol^{-1}\,cm^{-1}$)): 270 sh (7610), 395 (3560), 502 (305). ^{1}H NMR (C_4D_8O, ppm): 7.94 (2H, d, $J = 8.2$ Hz, ArH); 7.65 (2H, d, $J = 8.4$ Hz, ArH); 4.17–4.11 (2H, m, *endo*-methylene protons); 4,04–3.98 (2H, m, *endo*-methylene protons) 3.10–2.99 (2H, m, *exo*-methylene proton); 2.18–2.08 (2H, m, *exo*-methylene proton). ^{13}C NMR (C_4D_8O, ppm): 166.5, 151.1, 133.7, 128.5, 46.6, 43.2. Mass spectrum requires for $C_{11}H_{13}O_3ReS_4Na$ 531, found $[M+Na]^+$ 531.

2.5.2. [ReO{η^3-($SCH_2CH_2SCH_2CH_2S$)}{η^1-($C_6H_4CONHCH_2COOEt$-4-S)}] (**6**)

N-*p*-Mercaptobenzoyl glycine ethyl ester (**4a)** was used as the monothiol. Recrystallization from the mixture of dichloromethane and *n*-hexane gave the title complex **6** as a red solid (yield: 0.105 g, 71%). *Anal.* Calc. for $C_{15}H_{20}NO_4ReS_4$: C, 30.39; H, 3.40; N, 2.36. Found: C, 30.62; H, 3.54; N, 2.21%. IR (KBr, cm^{-1}) 1747 (vs, ester C=O), 1640 (vs, amide C=O), 963 (vs, Re=O). UV–Vis (CH_2Cl_2, λ/nm, (ε/$dm^3\,mol^{-1}\,cm^{-1}$)): 267sh (8960), 296 (5640), 395 (3540), 500 (280). ^{1}H NMR (CD_2Cl_2, ppm): 7.78 (2H, d, $J = 8.2$ Hz, ArH); 7.71 (2H, d, $J = 8.2$ Hz, ArH); 6.68 (1H, br s, –N*H*); 4.28–4.19 (6H, m, –O$CH_2$$CH_3$, –NH$CH_2$ and *endo*-methylene proton); 4.00–3.96 (2H,m, *endo*-methylene proton); 3.16–3.06 (2H, m, *exo*-methylene proton); 2.09–1.98 (2H, m, *exo*-methylene proton); 1.30 (3H, t, J=7.2 Hz, –O$CH_2$$CH_3$). ^{13}C NMR ($CD_2Cl_2$, ppm): 170.6, 167.1, 135.2, 132.8, 127.2, 61.9, 48.0, 44.4, 42.4, 14.6. Mass spectrum requires for $C_{15}H_{20}NO_4ReS_4Na$ 616, found $[M+Na]^+$ 616.

2.5.3. [ReO{η^3-($SCH_2CH_2SCH_2CH_2S$)}{η^1-($C_6H_4CONHCH(CH_3)COOEt$-4-S)}] (**7**)

N-*p*-Mercaptobenzoyl-L-alanine ethyl ester (**4b)** was used as the monothiol. The title complex **7** was recrystallized from the mixture of dichloromethane and *n*-hexane (yield: 0.088 g, 58%) *Anal.* Calc. for $C_{16}H_{22}NO_4ReS_4$: C, 31.66; H, 3.66; N, 2.31. Found: C, 31.78; H, 3.60; N, 2.42%. IR (KBr, cm^{-1}) 1735 (vs, ester C=O), 1630 (vs, amide C=O), 960 (vs, Re=O). UV–Vis (CH_2Cl_2, λ/nm, (ε/$dm^3\,mol^{-1}\,cm^{-1}$)): 266sh (16530), 293sh (10520), 395 (5730), 500 (550). ^{1}H NMR (CD_2C_2Cl, ppm): 7.78 (2H, d, $J = 8.4$ Hz, ArH); 7.71 (2H, d, $J = 8.4$ Hz, ArH) 6.73 (2H, d, $J = 7.2$ Hz, –N*H*); 4.77–4.63 (1H, m, –NHC*H*); 4.33–4.17 (4H, m, –O$CH_2$$CH_3$ and *endo*-methylene proton); 4.00–3.91 (2H, m, *endo*-methylene proton); 3.17–2.98 (2H, m, *exo*-methylene proton); 2.09–1.99 (2H, m, *exo*-methylene proton); 1.51 (3H, d, $J = 7.2$ Hz, –CHCH_3), 1.30 (3H, t, $J = 7.2$ Hz, –O$CH_2$$CH_3$). ^{13}C NMR ($CD_2Cl_2$, ppm): 173.6, 166.6, 135.2, 133.0, 128.3, 127.1, 62.1, 49.2, 48.0, 44.4, 18.9, 14.6. Mass spectrum requires for $C_{16}H_{22}NO_4ReS_4Na$ 629.9, found $[M+Na]^+$ 629.8.

2.5.4. [ReO{η^3-($SCH_2CH_2SCH_2CH_2S$)}{η^1-($C_6H_4CONHCH(CH_2Ph)COOEt$-4-S)}] (**8**)

N-*p*-Mercaptobenzoyl-L-phenylalanine ethyl ester (**4c)** was used as the monothiol. Recrystallization from the mixture of dichloromethane and *n*-hexane gave the title complex **8** as a red solid (yield: 0.115 g, 67%). *Anal.* Calc. for $C_{22}H_{26}NO_4ReS_4$: C, 38.69; H, 3.84; N, 2.05. Found: C, 38.38; H, 3.98; N, 2.23%. IR (KBr, cm^{-1}) 1740 (vs, ester C=O), 1630 (vs, amide C=O), 962 (vs, Re=O). UV–Vis (CH_2Cl_2, λ/nm, (ε/$dm^3\,mol^{-1}\,cm^{-1}$)): 265sh (12547), 295sh (8005), 396 (4940), 505 (470). ^{1}H NMR (CD_2C_2, ppm): 7.69 (4H, s, ArH); 7.35–7.18 (5H, m, Ph); 6.58 (1H, d, $J = 7.2$ Hz, –N*H*); 5.04–4.98 (1H, m, –NHC*H*); 4.25–4.16 (4H, m, –O$CH_2$$CH_3$ and *endo*-methylene proton); 4.00–3.95 (2H, m, *endo*-methylene proton); 3.32–3.06 (4H, m, -CHCH_2Ph and *exo*-methylene proton); 2.09–1.99 (2H, m, *exo*-methylene proton); 1.27 (3H, t, $J = 7.2$ Hz, –O$CH_2$$CH_3$). ^{13}C NMR ($CD_2Cl_2$, ppm): 172.0, 166.7, 150.6, 136.8, 135.2, 133.0, 129.0, 127.5, 127.1, 62.2, 49.2, 48.0, 44.4, 38.5, 14.6. Mass spectrum requires for $C_{22}H_{26}NO_4ReS_4Na$ 706, found $[M+Na]^+$ 706.

2.6. Crystallographic measurements and structure determination

Dark green block of complex **5** was mounted on a glass fiber. Intensity measurements were carried out on a Rigaku RAXIS RAPID imaging plate area detector system with

Table 1
Crystallographic data for complex **5**

Parameter	Complex **5**
Formula	$C_{11}H_{13}O_3ReS_4$
Formula Weight	507.67
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	8.438(4)
b (Å)	12.488(6)
c(Å)	14.062(5)
α (°)	90.00
β (°)	95.45(3)
γ (°)	90.00
Volume (Å^3)	1475.1(11)
Z	4
Temperature (K)	173 (1)
D_{calc} (g cm^{-3})	2.286
μ (mm^{-1})	8.802
F(000)	968
λ(Mo K$_\alpha$) (Å)	0.7107
Crystal size (mm)	$0.20 \times 0.10 \times 0.10$
θ Range for data collection (°)	$0.0 < \theta < 27.4$
Reflections measured	14086
Reflections independent (R_{int})	3356 (0.028)
Reflections observed ($I > 2\sigma$)	2855
R[a]	0.018
WR_2[b]	0.042
Goodness of fit	1.02

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

Mo K_α radiation from a graphite monochromator ($\lambda = 0.71075$ Å) at a temperature of −100 °C. Crystal data collection and final refinement parameters are summarized in Table 1. The structures were solved by direct methods (SIR-92) [38] or heavy-atom Patterson methods [39], and expanded using Fourier techniques [40]. The non-hydrogen atoms were refined using anisotropic temperature factors. Hydrogen atoms were introduced at calculated positions using the riding model. All calculations were performed using the crystal structure crystallographic software package [41,42].

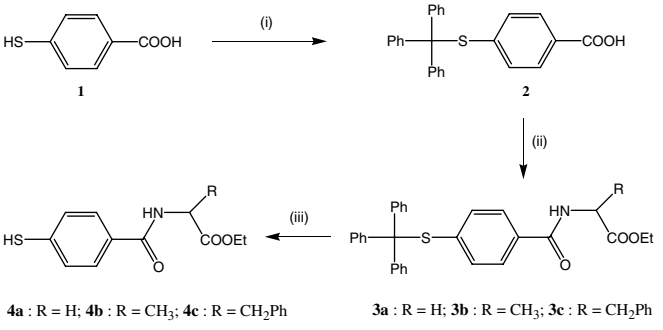
3. Results and discussion

3.1. Syntheses and characterization of ligands (*4a, 4b, and 4c*)

Thiol group of *p*-mercaptobenzoic acid was protected and deprotected by using the procedure slightly modified on the basis of previously reported method [43]. The thiol protected benzoic acid was coupled with the free N-terminal amino acid esters of glycine, L-alanine, and L-phenylalanine by using DCC and HOBt under basic conditions, and deprotected by TFA. The resulting *N-p*-mercaptobenzoyl amino acid esters (**4a**, **4b**, and **4c)** were obtained as white solids (Scheme 1). Their structures were confirmed to be the proposed ones from the results of elemental analyses, and IR, ^{1}H NMR, ^{13}C NMR, and mass spectrometric measurements.

The most important features in the IR spectra of **4a**, **4b**, and **4c** are the existence of strong bands in the ranges of 2555–2560, 1725–1740, and 1625–1640 cm^{-1}, which are assigned to *ν*(H–S), *ν*(ester C═O), and *ν*(amide C═O) stretching vibrations, respectively [44,45].

^{1}H NMR spectra of **4a**, **4b**, and **4c** in CD_2Cl_2 show one singlet at 3.73, 3.71, and 3.68 ppm, and a triplet ($J = 7.2$) at 1.29, 1.29, and 1.26 ppm, respectively, in which the former and the latter are assigned to the thiol group attached to the disubstituted benzoyl ring and the methyl group of –OCH_2CH_3, respectively. The protons of *p*-disubstituted benzoyl group appear as two doublets in the region of 7.15–7.66 ppm, e.g., in the glycine derivative **4a** the aromatic protons are present as two doublets at 7.33 and 7.66 ppm, respectively. The N*H* proton is observed as a broad single/doublet in the range of 6.80–6.86 ppm.



Scheme 1. Syntheses of *N-p*-mercaptobenzoyl amino acid ethyl esters **4a**–**c**; (i) Ph_3C–Cl, DMF; (ii) DCC, HOBt, Et_3N, amino acid ethyl ester; (iii) TFA, TES.

The ^{13}C NMR spectra of **4a**, **4b**, and **4c** show signals in the region of 166–173 ppm, which are assigned as amide C═O and ester C═O groups, respectively. The methylene and methyl carbon atoms of the ethyl ester groups are observed in the narrow ranges of 62.4–62.2 and 14.5–14.5 ppm, respectively. A complete assignment of the ^{1}H NMR and ^{13}C NMR spectra of *N-p*-mercaptobenzoyl glycine ethyl ester **4a** is presented in Table 2 as a typical example.

The ESIM spectra displayed species $[M + Na]^+$ for compounds (**2**, **3a**–**c**, **4a**–**c**, and **5**–**8**). The isotopic distribution patterns of peaks of $[M+Na]^+$ ion for compounds (**2**, **3a**–**c**, **4a**–**c**, and **5**–**8**) are same as those theoretically expected.

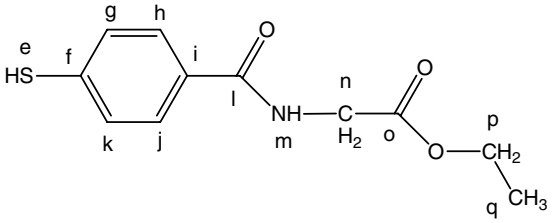
3.2. Syntheses and characterization of the complexes (*5–8*)

The [ReO(SSS)Cl] complex as a starting material was synthesized according to the procedure reported by Fietz et al. [5]. Reactions of **1**, **4a**, **4b**, and **4c** with the complex [ReO(SSS)Cl] in the presence of triethylamine as the deprotonating agent afforded the mixed ligand complexes **5**–**8** (Scheme 2).

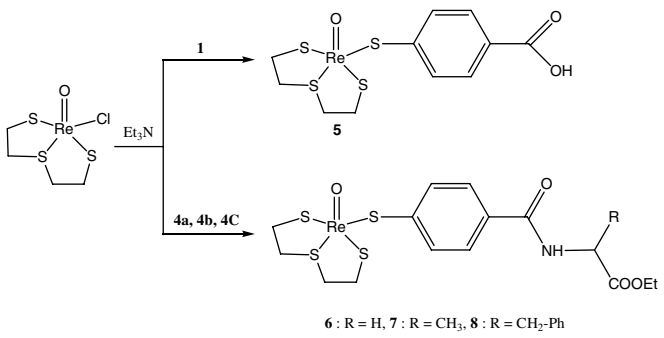
All complexes reported here are fairly stable even in the presence of air and moisture in both solid and liquid phases. Complexes **6**–**8** are soluble in various organic solvents (e.g., dichloromethane, acetone, methanol, ethanol, acetonitrile, nitromethane, and DMF). Complex **5** is soluble in THF and DMF, and not soluble in any other common organic solvents. Only complex **5** was crystallized from THF solution and its X-ray crystal structure is described in crystallography part.

Infrared spectra of complexes **5**, **6**, **7**, and **8** have strong bands at 967, 963, 960, and 962 cm^{-1}, respectively, which are assigned to *ν*(Re═O) stretching. These values are com-

Table 2
^{1}H and ^{13}C NMR spectroscopic data for **4a**



Site	^{1}H NMR	^{13}C NMR
e	3.73(s)	
f		130.5
g,k	7.33(d)	128.4
h,j	7.66(d)	129.0
i		138.1
l		168.3
m	6.86(br s)	
n,p	4.27–4.17(m)	62.4, 42.6
o		170.3
q	1.29(t)	14.5



Scheme 2. Syntheses of complexes **5**, **6**, **7**, and **8**.

patible with those (930–980 cm^{-1}) observed in the other '3+1' oxo-Re(V) complexes [4–15]. Another common feature of IR spectra of complexes **6**–**8** is to show very strong bands in the ranges of 1735–1747 and 1630–1640 cm^{-1}, which are due to the carbonyl stretching vibrations of ester and amide, respectively. These carbonyl stretching bands are almost consistent with those of free ligands, **4a**–**4c**. This means that the carbonyl oxygen does not coordinate to Re(V). Furthermore, complexes **5**–**8** have no bands around 2555–2560 cm^{-1}, which correspond to the H–S stretching vibration observed in **4a**–**4c**. This indicates the S-coordination of ligands **1**, **4a**, **4b**, and **4c**. Assignments of the IR spectra for ligand **4a** and complex **6** are presented in Fig. 1 as typical examples.

^{1}H NMR signals of the *p*-disubstituted benzoyl group were observed as two doublets in the range of 7.71–8.01 ppm for complexes **5**–**7** and as a singlet at 7.69 for complex **8**. The amide NH proton signals were detected as a doublet or a broad singlet in the region of 6.58–6.73 ppm. ^{1}H and ^{13}C NMR spectra were assigned based on ^{1}H/^{1}H COSY spectra as previously reported by us [46]. The methylene proton signals in the chelate ring SSS are strongly coupled with each other. Protons on the coordinated SSS are identified as *endo* (protons are closer to oxygen of Re=O core) and *exo* (remote from oxygen atom of Re=O core) [6,47]. The *endo* protons are more strongly deshielded than those of *exo* protons, because the *endo* protons interact more strongly with π cloud of Re=O. Therefore, ^{1}H NMR signals of *endo* protons should appear at lower field compared to the *exo* ones. The multiple signals in the ranges of 4.11–4.33, 3.91–4.04, 2.98–3.32, and 1.98–2.18 ppm for complexes **5**–**8** are assigned as the *endo*-terminal, *endo*-inside, *exo*-terminal, and *exo*-inside methylene protons, respectively. The difference in chemical shifts between the *endo*- and *exo*-methylene groups on the coordinated SSS is comparable with the literature [48]. Complete assignments of the ^{1}H NMR spectra for complexes **5** and **6** are presented in Fig. 2. In ^{13}C NMR spectra of complexes **6**–**8**, signals were observed in the regions of 166.6–167.1, 127.1–135.3, and 43.8–48.0 ppm, which are assigned as amide carbonyl carbon, the carbon of the disubstituted benzoyl ring, and the methylene carbon of the coordinated SSS, respectively. The methylene carbon signals of SSS are comparable with those for the complexes reported previously [49].

From these results, complexes **5**–**8** have structures with configuration shown in Scheme 2.

3.3. X-ray diffraction study

Suitable single crystals for X-ray structural analysis were obtained for complex **5**. ORTEP view is shown in Fig. 3, and selected bond lengths and angles for complex **5** are listed in Table 3. The trigonality index (τ) [10,50] of complex **5** was evaluated based on the definition, $\tau = (\beta - \alpha)/60$, where β and α are the largest angle and the second larg-

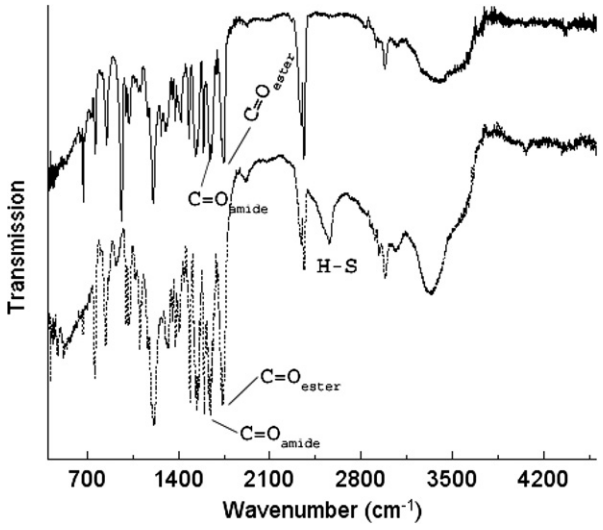


Fig. 1. IR spectra of ligand **4a** (...) and complex **6** (—) with KBr at room temperature.

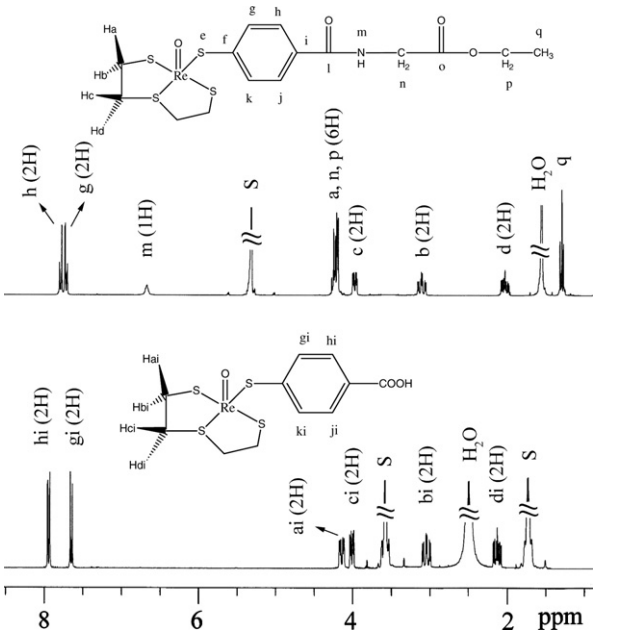


Fig. 2. ^{1}H NMR spectra of complex **6** (a) in CD_2Cl_2 and complex **5** (b) in C_4D_8O at room temperature. The peaks marked as S are due to the solvents.

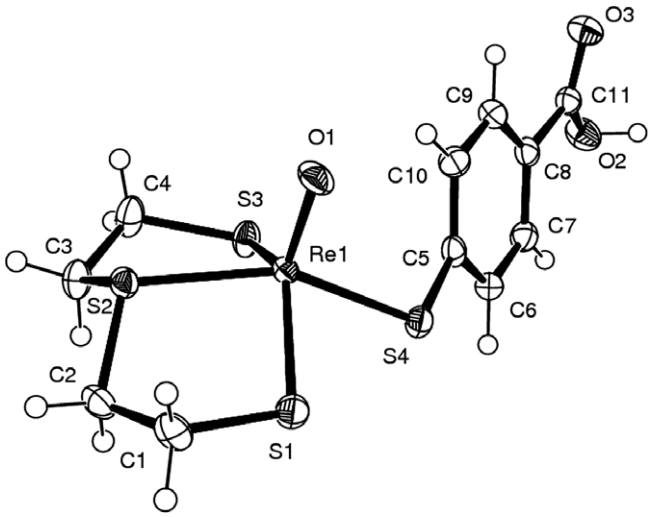


Fig. 3. ORTEP drawing of complex **5** with the atom numbering scheme; thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were introduced in calculated positions.

Table 3
Selected bond lengths (Å) and angles (°) of complex **5**

Re1–O1	1.685(3)	Re1–S1	2.297(2)
Re1–S2	2.364(2)	Re1–S3	2.296(1)
Re1–S4	2.326(2)	S4–C5	1.768(4)
S1–Re1–S2	84.35(4)	S2–Re1–S3	84.02(4)
S1–Re1–S4	81.66(4)	S3–Re1–S4	86.86(4)
S1–Re1–O1	113.38(12)	S2–Re1–O1	103.27(9)
S3–Re1–O1	115.86(12)	S4–Re1–O1	104.64(9)
S1–Re1–S3	130.76(5)	S2–Re1–S4	151.90(4)
Re1–S4–C5	111.40(13)		

est angle of central metal atom with surrounded donor atoms, respectively, and the τ value is equal to 0 for a square pyramid and 1 for a trigonal bipyramid. The angles corresponding to β and α in complex **5** are (S2–Re1–S4) and (S1–Re1–S3), and are 151.90(4)° and 130.76(5)°, respectively. Hence, the τ value of complex **5** is 0.352. This suggests that the structure of complex **5** is distorted square pyramidal rather than distorted trigonal bipyramidal. The Re=O bond distance of complex **5** is 1.685(3) and is comparable to Re=O distances (1.67–1.74 Å) observed for other [Re(SSS)S] complexes [10,11,14,32]. The basal plane is formed by the sulfur atoms of the tridentate ligand and unidentate thiol, while the apical position is occupied by the remaining oxo group. The Re atom of complex **5** lies above the basal plane towards the apex oxygen atom of Re=O (0.96 Å). The dihedral angles formed by the chelating atoms of the tridentate ligands are −79.01° and 51.49° for S1–C1–C2–S2 and S2–C3–C4–S3, respectively. The bond length of Re1–S2 is 2.364(2) Å, and is slightly longer than those (2.297(2), 2.296 Å) of Re1–S1 and Re1–S3. The distance of Re1–S4 is 2.326(2) Å and is in the range of the corresponding distances observed in the other [ReO(SSS)S] complexes [10,11,14,32]. In unit cell, two molecules of complex **5** are associated by using intermolecular hydrogen bonds linking through carboxylic acids. This is a common phenomenon for non-coordinated carboxylic acids in solid state [51,52]. The bond distance and bond angle of the hydrogen bond are O2–H13···O3 = 2.644(5) Å and 103.2(3)°.

4. Conclusion

The oxo-Re(V) '3+1' mixed ligand complexes (**6**–**8**) with 3-thiopentane-1,5-dithiolate and functional *N*-*para*-mercaptobenzoyl amino acid ethyl esters (**4a**–**c**) were synthesized. The ligands **4a**–**c** were prepared by the coupling of *p*-mercaptobenzoic acid with the amino acid ethyl esters using the conventional 1,3-dicyclohexylcarbodiimide (DCC) and 1-hydroxy-benzotriazole (HOBt) protocol. The molecular structure of complex **5** with η^1-(C_6H_4COOH-4-S) as the basic moiety of ligands **4a**–**c** was determined to be a distorted square pyramidal by using single crystal X-ray analytical method.

Acknowledgement

This work has been supported by the Japan Society for Promotion of Science (JSPS).

Appendix A. Supplementary data

CCDC 619181 contains the supplementary crystallographic data for [ReO{η^3-($SCH_2CH_2SCH_2CH_2S$)}{η^1-(C_6H_4COOH-4-S)}]. 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.ica.2007.06.038.

References

[1] J. Ehrhardt, A.R. Ketring, T.A. Turpin, M.S. Razavi, J.L. Vanderheyden, F.M. Su, A.R. Fritzberg, in: M. Nicolini, G. Bandoli, U. Mazzi (Eds.), Technetium and Rhenium in Chemistry and Nuclear Medicine 3, Cortina International, Verona, 1990.
[2] J.R. Dilworth, S.J. Parrott, Chem. Soc. Rev. 27 (1998) 43.
[3] W.A. Volkert, T.J. Hoffman, Chem. Rev. 99 (1999) 2269.
[4] H. Spies, T. Fietz, H.-J. Pietzsch, B. Johannsen, P. Leibnitz, G. Reck, D. Scheller, K. Klostermann, J. Chem. Soc., Dalton Trans. (1995) 2277.
[5] T. Fietz, H. Spies, H.-J. Pietzsch, P. Leibnitz, Inorg. Chim. Acta 231 (1995) 233.
[6] M.S. Papadopoulos, I.C. Pirmettis, M. Pelecanou, C.P. Raptopoulou, A. Terzis, C.I. Stassinopoulou, E. Chiotellis, Inorg. Chem. 35 (1996) 7377.
[7] K.P. Maresca, F.J. Femia, J.W. Babich, J. Zubieta, Inorg. Chem. Commun. 1 (1998) 209.
[8] T. Maina, C. Tsoukalas, G. Patsis, I. Pirmettis, B. Nock, M. Papadopoulos, C. Raptopoulou, A. Terziz, E. Chiotellis, Polyhedron 18 (1999) 3545.

[9] M. Papadopoulos, C. Tsoukalas, I. Pirmettis, B. Nock, T. Maina, Z. Abedin, C.P. Raptopoulou, A. Terzis, E. Chiotellis, Inorg. Chim. Acta 285 (1999) 97.
[10] K.P. Maresca, G.H. Bonavia, J.W. Babich, J. Zubieta, Inorg. Chim. Acta 284 (1999) 252.
[11] K.P. Maresca, F.J. Femia, G.H. Bonavia, J.W. Babich, J. Zubieta, Inorg. Chim. Acta 297 (2000) 98.
[12] F.J. Femia, X. Chen, K.P. Maresca, T.M. Shoup, J.W. Babich, J. Zubieta, Inorg. Chim. Acta 306 (2000) 30.
[13] X. Chen, F.J. Femia, J.W. Babich, J. Zubieta, Inorg. Chim. Acta 307 (2000) 88.
[14] K.P. Maresca, T.M. Shoup, F.J. Femia, M.A. Burker, A. Fischman, J.W. Babich, J. Zubieta, Inorg. Chim. Acta 338 (2002) 149.
[15] M. Friebe, H. Spies, W. Seichter, P. Leibnitz, B. Johannsen, J. Chem. Soc., Dalton Trans. (2000) 2471.
[16] I.R. Baird, R. Mosi, M. Olsen, B.R. Cameron, S.P. Fricker, R.T. Skerji, Inorg. Chim. Acta 59 (2006) 2736.
[17] R. Mosi, I.R. Baird, J. Cox, V. Anastassov, B. Cameron, R.T. Skerlj, S.P. Fricker, J. Med. Chem. 49 (2006) 5262.
[18] B. Johannsen, H.-J. Pietzsch, Eur. J. Nucl. Med. 29 (2002) 263.
[19] B. Johannsen, M. Scheunemann, H. Spies, P. Brust, J. Wober, R. Syhre, H.-J. Pietzsch, Nucl. Med. Biol. 23 (1996) 429.
[20] D. Papagiannopoulou, I. Pirmettis, T. Maina, M. Pelecanou, A. Nikolopoulou, E. Chiotellis, C.P. Raptopoulou, A.T. Vlahos, V.A. Terzis, M. Papadopoulos, E. Chiotellis, J. Biol. Inorg. Chem. 6 (2001) 256.
[21] A. León, A. Rey, L. Mallo, I. Pirmettis, M. Papadopoulos, E. León, M. Pagano, E. Manta, M. Incerti, C. Raptopoulou, A. Terzis, E. Chiotellis, Nucl. Med. Biol. 29 (2002) 217.
[22] J. Giglio, A. Rey, H. Cerecetto, I. Pirmettis, M. Papadopoulos, E. León, A. Monge, A.L. de Ceráin, A. Azqueta, M. González, M. Fernández, A. Paolino, A. León, Eur. J. Med. Chem. 41 (2006) 1144.
[23] F. Wüst, D. Scheller, H. Spies, B. Johannsen, Eur. J. Inorg. Chem. (1998) 789.
[24] M.B. Skaddan, J.A. Katzenellenbogen, Bioconjugate Chem. 10 (1999) 119.
[25] A. Zablotskaya, I. Segal, S. Germane, I. Shestakova, E. Lukevics, T. Kniess, H. Spies, Appl. Organometal. Chem. 16 (2002) 550.
[26] J.E. Cyr, D.A. Pearson, D.M. Wilson, C.A. Nelson, M. Guaraldi, M.T. Azure, J. Lister-James, L.M. Dinkelborg, R.T. Dean, J. Med. Chem. 50 (2007) 1354.
[27] R. Syhre, S. Seifert, H. Spies, A. Gupta, B. Johannsen, Eur. J. Nucl. Med. 25 (1998) 793.
[28] B. Nock, T. Maina, D. Yannoukakos, I.C. Pirmettis, M.S. Papadopoulos, E. Chiotllis, J. Med. Chem. 42 (1999) 1066.
[29] B. Nock, T. Maina, A. Tsortos, M. Pelecanou, C.P. Raptopoulou, M. Papadopoulos, H.-J. Pietzsch, C.I. Stassinopoulou, A. Terzis, H. Spies, G. Nounesis, E. Chiotellis, Inorg. Chem. 39 (2000) 4433.
[30] X. Chen, F.J. Femia, JW. Babich, J. Zubieta, Inorg. Chim. Acta 307 (2000) 154.
[31] J.D. Correia, Â. Domingos, I. Santos, H. Spies, J. Chem. Soc., Dalton Trans. (2001) 2245.
[32] E. Palma, J.D.G. Correia, Â. Domingos, I. Santos, Eur. J. Inorg. Chem. (2002) 2402.
[33] C. Fernandes, L. Patrício, R. Moreira, G. Cantinho, H. Pena, P.C. Campello, I. Santos, Nucl. Med. Biol. 31 (2004) 139.
[34] C. Fernandes, T. Kniess, L. Gano, S. Seifert, H. Spies, I. Santos, Nucl. Med. Biol. 31 (2004) 785.
[35] C. Fernandes, J.D.G. Correia, L. Gano, I. Santos, S. Seifert, R. Syhre, R. Bergmann, H. Spies, Bioconjugate Chem. 16 (2005) 660.
[36] C. Tsoukalas, M.S. Papadopoulos, T. Maina, I.C. Pirmettis, B.A. Nock, C. Raptopoulou, A. Terzis, E. Chiotellis, Nucl. Med. Biol. 26 (1999) 297.
[37] C. Tsoukalas, I. Pirmettis, G. Patsis, A. Papadopoulos, C.P. Raptopoulou, A. Terzis, M. Papadopoulos, E. Chiotellis, Nucl. Med. Biol. 28 (2001) 975.
[38] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. Burla, G. Polidori, M. Camalli, J. Appl. Crystallogr. 27 (1994) 435.
[39] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smits, C. Smykalla, The DIRDIF Program System: Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.
[40] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits, The DIRDIF-99 Program System: Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1999.
[41] CRYSTALSTRUCTURE 3.10: Crystal Structure Analysis Package, Rigaku and Rigaku/MSC, 2000–2002.
[42] D.J. Watkin, C.K. Prout, J.R. Carruthers, P.W. Betteridge, CRYSTALS Issue 10 Chemical, Crystallography Laboratory, Oxford, UK.
[43] K. Ogawa, T. Mukai, Y. Arano, M. Ono, H. Hanaoka, S. Ishino, K. Hashimoto, H. Nishimura, H. Saji, Bioconjugate Chem. 16 (2005) 751.
[44] A.S.N. Murthy, C.N.R. Rao, B.D.N. Rao, P. Venkateswarlu, Trans. Faraday Soc. (1962) 855.
[45] S.M. Rozenberg, T. Nishio, T. Steiner, New J. Chem. 23 (1999) 585.
[46] S. Chowdhury, N. Koshino, A. Canlier, K. Mizuoka, Y. Ikeda, Inorg. Chim. Acta 359 (2006) 2472.
[47] M.S. Papadopoulos, M. Pelecanou, I.C. Pirmettis, D.M. Spyriounis, C.P. Raptopoulou, A. Terzis, C.I. Stassinopoulou, E. Chiotellis. Inorg. Chem. 35 (1996) 4478.
[48] G.E.D. Mullen, P.J. Blower, D.J. Price, A.K. Powell, M.J. Howard, M.J. Went, Inorg. Chem. 39 (2000) 4093.
[49] A.W. Addision, T.N. Rao, J. Reedijik, J.V. Rijin, G.C. Verschool, J. Chem. Soc., Dalton Trans. (1984) 1349.
[50] M. Li, A. Ellern, J.H. Espenson, Inorg. Chem. 44 (2005) 3690.
[51] J.L. Derissen, P.H. Smit, Acta Crystallogr., Sect. A 34 (1978) 842.
[52] R.A. Lalancette, H.W. Thompson, Acta Crystallogr., Sect. C 59 (2003) o274.