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Synthesis and characterization of monooxorhenium(V) complexes of mercaptoacetylglycylglycylglycine. Crystal structure of tetrabutylammonium oxo(mercaptoacetylglycylglycylglycine)rhenate(V)

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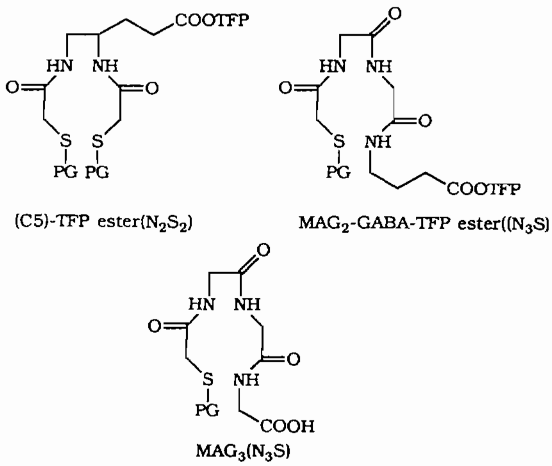
Abstract

A stable complex of rhenium(V) with mercaptoacetylglycylglycylglycine (MAG_3) was prepared by the reaction of $ReO_2(en)_2Cl$ (en = ethylenediamine) or Re(V) citrate with MAG_3 at pH 10.0. The complex was isolated as salts of $X[ReO(MAG_3)]$ where $X = Bu_4N^+$, Ph_4As^+. $Ph_4As[ReO(MAG_3)]$ was characterized by IR, UV–Vis spectroscopy, elemental analysis and mass spectroscopy. $Bu_4N[ReO(MAG_3)]$ was characterized by NMR and single crystal X-ray structure determination. $Bu_4N[ReO(MAG_3)]$ crystallizes in space group $Pna2_1$, with cell constants $a = 17.902(3)$, $b = 9.029(2)$, $c = 18.741(3)$ Å, $V = 3029(1)$ Å^3 and $Z = 4$. The structure was refined to a final R value of 0.046 and contains discrete $[ReO(MAG_3)]^-$ and Bu_4N^+ ions. The rhenium atom in $[ReO(MAG_3)]^-$ is bound to three nitrogens (amide), one sulfur (thiolate), and one oxygen (yl) atom in a distorted square pyramidal geometry. The oxygen atom forms the apex of the square pyramid with a Re–O bond distance of 1.68(1) Å. The average Re–N bond distance is 2.00 ± 0.02 Å and the Re–S bond is 2.29(1) Å.

Introduction

The potential radiotherapeutic applications of ^{186}Re (1.07 MeV beta max, 3.7 d half life, 137 keV gamma photons (9%)), and ^{188}Re (2.12 MeV beta max, 0.9 d half life, 155 keV gamma photons (15%)) have stimulated interest in the chemistry of rhenium [1, 2]. Potential applications under development using these two radioisotopes are palliation of pain due to bone metastases with a rhenium complex of ethane-1-hydroxy-1,1-diphosphonate [3], treatment of arthritis via synovial joint administration [4], and antibody targeted therapy for tumors [5].

Recently we have developed methods to specifically radiolabel antibodies with technetium-99m by a preformed chelate method [6, 7] for the staging of cancer via gamma camera imaging. The radiolabeling process involves complexing the metal as the $Tc{=}O^{3+}$ core with a diamide dithiol (N_2S_2) or a triamide thiol (N_3S) bifunctional chelating agent (Fig. 1) and then conjugating the metal chelate to the antibody via



PG = PROTECTING GROUP

Fig. 1. Structures of MAG_3 and related ligands.

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reaction of an active ester group with amine groups on the antibody. The resultant antibody–^{99m}Tc–N_2S_2 or N_3S conjugate has been shown to be very stable both *in vivo* and *in vitro*. Based on the periodic relationship and the identical structures of the Tc and Re–N_2S_2 complexes [8], we have extended the same methodology to label antibodies with ^{186}Re for the treatment of cancer [9]. After evaluation of several N_2S_2 and N_3S ligands, phase I therapy clinical trials have been initiated using antibodies labeled by conjugation with the N_3S active ester complex (MAG_2GABA TFP, Fig. 1) [10].

This N_3S amide thiol class of chelating agent was chosen for rhenium because the initial ligand of the class, mercaptoacetylglycylglycylglycine (MAG_3), was reported to form a stable technetium(V) complex [11] that is rapidly and specifically excreted from the body via the kidneys. This is desirable as a means of eliminating non-targeted therapeutic radiation from the body. Currently the technetium complex, $^{99m}TcO(MAG_3)$ is in routine clinical use as a renal tubular function radiopharmaceutical [12].

Until now, there have been no reports on the preparation and characterization of a rhenium(V) complex of any chelating agent containing triamide thiol donor atoms. Because of the importance of the use of radiolabeled N_2S_2/N_3S chelates in radiotherapy and the analogy of chemistry of rhenium with technetium, we prepared and characterized the MAG_3 complex of rhenium and report the results in this paper. This is the first report of a structural characterization of a rhenium(V)–N_3S complex and the results substantiate the utility of the N_3S chelating agents to attach ^{186}Re to antibodies to provide a stable Re–N_3S–antibody conjugate.

Experimental

All chemicals used were of reagent grade. NH_4ReO_4 was obtained from Aldrich Chemical Company. Infrared spectra were recorded in the range 4000–200 cm^{-1} in a nujol mull by a Perkin-Elmer P2A3 instrument. UV–Vis spectra were recorded by an HP8451A diode array spectrophotometer. Mass spectra (FAB, negative ion) were recorded on a Varian 731 instrument in glycerol matrix with $CHCl_3$ as solvent. NMR spectra were recorded in $CDCl_3$ on a Bruker WM-500 HMZ instrument. HPLC was performed with a C_{18} column (5 μ, 4.6×250 mm, Beckman) on Beckman models 110 and 113 systems equipped with a UV detector (254 nm). The detectors were equipped with Hewlett-Packard 3390A integrating recorders. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Preparation of $ReO_2(en)_2Cl$

This complex was prepared as described in ref. 13.

Synthesis of benzoylmercaptoacetylglycylglycylglycine

This compound was prepared as described in ref. 14.

Preparation of $Ph_4As[ReO(MAG_3)]$

A solution of mercaptoacetylglycylglycylglycine was prepared by heating 116 mg (0.32 mmol) of benzoylmercaptoacetylglycylglycylglycine in 5 ml of 0.1 N NaOH at 90 °C for 15 min under nitrogen. Then, 120 mg (0.32 mmol) of $ReO_2(en)_2Cl$ dissolved in 5 ml of H_2O was added to the solution of the ligand. The pH of the reaction mixture was adjusted to 10.0 and the solution heated at 90 °C for 90 min. The solution was allowed to cool to room temperature, the pH was adjusted to 3.0 with 1 N HCl, and filtered. To this clear orange solution, 140 mg (0.33 mmol) of Ph_4AsCl in 2 ml of water was added. The complex was then extracted into chloroform. The organic layer was separated, dried with anhydrous sodium sulfate, and filtered. After evaporation of solvent, the orange oil residue was dissolved in 2 ml of ethanol. Then 10 ml of ethyl ether was added, and the side of the beaker scratched with a glass rod. The precipitated light orange solid was centrifuged, washed with ether, and dried *in vacuo* over $CaSO_4$. After recrystallization from ethanol/H_2O, 140 mg of the complex were obtained (50% yield). *Anal.* Calc. for $C_{32}H_{29}AsN_3O_6SRe$:C, 45.55; H, 3.44; N, 4.98; S, 3.80. Found: C, 45.61; H, 3.71; N, 4.92; S, 3.89%. UV–Vis spectrum in CH_3CN, nm (ϵ in l mol^{-1} cm^{-1}): 480sh (45), 402 (170), 264 (905). IR: 975 cm^{-1} (Re=O). FAB-MS (negative ion) M^-: 460, 462.

Preparation of $(Bu_4N)[ReO(MAG_3)]$

The procedure was similar to that of Ph_4As-$[ReO(MAG_3)]$ except that Bu_4NCl was used instead of Ph_4AsCl. Orange colored crystals of the complex were obtained by diffusing diethyl ether into a solution of the compound in ethanol. ^1H NMR 500 MHz ($CDCl_3$): 5.5, 4.74 (dd, 2H, NCH_2, J=14.9 Hz) 4.94, 4.52 (dd, 2H, NCH_2, J=18.6 Hz), 4.38, 4.37 (dd, 2H, NCH_2, J=18.2 Hz), 4.05, 3.78 (dd, 2H, SCH_2, J=17.1 Hz), 3.14 (m, 8H, $N(CH_2)_4$, butyl), 1.59 (m, 8H, $(CH_2)_4$, butyl), 1.43 (m, 8H $(CH_2)_4$, butyl), 1.01 (m, 12H, $(CH_3)_4$, butyl).

Preparation of $[ReO(MAG_3)]^-$ from ReO_4^-, $SnCl_2$ and citric acid

After 7.78 mg (40 μmol) of $SnCl_2$ was dissolved in 1 ml of 0.5 M citric acid, a 1 ml solution of (10.6

mg, 40 μmol) of NH_4ReO_4 was added. Benzoylmercaptoacetylglycylglycylglycine (15.0 mg, 57 μmol) was dissolved in 2 ml of 0.1 N NaOH and heated under nitrogen at 90 °C for 10 min. The solution was then added to the Re(V) citrate solution. The pH of the reaction mixture was adjusted to 10.0 and heated at 90 °C for 60 min. Yield of $[ReO(MAG_3)]^-$ by HPLC (UV detection, retention volume 4.2 ml, flow rate: 1.0 ml/min, mobile phase: 2% CH_3CN 0.01 M phosphate pH = 7.0, C_{18}-reverse phase column) was 70%.

X-ray crystallographic studies

A crystal of dimensions 0.13×0.18×0.25 mm was used for data collection. Space group and approximate cell constants were obtained from the angular settings of 24 reflections in the 2θ range 15 to 44° on a CAD-4F diffractometer. Intensities were collected by ω–2θ scan up to resolution of $2\theta = 46°$. A total of 2180 reflections was collected of which 1588 were classified as observed $|F_o| \geq 4\sigma(|F_o|)$. Intensities of three reflections were monitored every three hours and there was no significant decay. Absorption corrections in the range 0.85 to 1.10 were applied empirically on the basis of azimuthal scans of six reflections whose chi angles were close to 90°.

The structure was solved by Patterson and Fourier methods and refined isotropically for all non-hydrogen atoms, except the rhenium atom which was refined anisotropically, with unit weights. Hydrogen atoms were not located. Final values of R and R_w and S (goodness of the fit) were 0.046, 0.053 and 2.36, respectively. The final difference map showed the maximum electron density of 0.8 $Å^{-3}$ near the rhenium atom. Scattering factors were from Cromer and Mann [15] and corrections for anomalous dispersion for rhenium and sulfur atoms were from the International Tables for Crystallography [16]. Calculations were performed with X-ray 76 crystallographic programs [17]. The experimental data for crystal structure determination are: formula $[N(C_4H_9)_4]^+$ $Re(C_8H_9O_6N_3S)^-$, molecular weight 703.90, orthorhombic, space group $Pna2_1$, $a = 17.902(3)$, $b = 9.029(2)$, $c = 18.741(3)$ Å, $V = 3029(1)$ $Å^3$, $Z = 4$, $D_{calc} = 1.543$ mg/ml, radiation Mo $K\alpha = 0.7107$ Å, $\mu = 4.35$ mm^{-1}, $F(000) = 1424$.

Results and discussion

$[ReO(MAG_3)]^-$ can be prepared by the ligand exchange reaction of $ReO_2(en)_2Cl$ or Re(V)-citrate with MAG_3. The maximum yield as determined by HPLC is obtained when the pH of the exchange reaction is 10. In contrast, the technetium complex has been prepared by direct reduction of TcO_4^- by dithionite in the presence of the ligand at pH = 10–12 [14]. Attempts to prepare the rhenium complex by this method were not successful because ReO_4^- is more difficult to reduce than TcO_4^- under the same conditions. The formation of salts like $X[ReO(MAG_3)]$ where $X = Ph_4As^+$ and Bu_4N^+ and the chemical analysis indicates that the ligand loses four protons upon complexation with rhenium and thus the overall charge on the oxocore (ReO^{3+} core) is negative, similar to the Tc complex [11].

Like the technetium complex, the complex is quite stable in solution and in the solid state as salts of Ph_4As^+ or Bu_4N^+ ions. In solution, no decomposition of the complex to ReO_2 or ReO_4^- was observed when heated to 100 °C in either acid (pH = 2.0) or base (pH = 11.0). The $[ReO(MAG_3)]^-$ complex thus appears to be as stable toward hydrolytic or oxidative decomposition as the analogous technetium complex in spite of the greater tendency of the reduced rhenium to be reoxidized to ReO_4^-. The complex can also be prepared starting from ReO_4^-, $SnCl_2$, citric acid and MAG_3 at low pH. This alternative method of preparing the same complex is useful in the preparation of $^{186}Re/^{188}Re$ radiopharmaceuticals since the starting form of radioactive rhenium is ReO_4^-. Spectral data supporting the structure of $[ReO(MAG_3)]$ were obtained.

The infrared spectrum of the complex shows a peak around 975 cm^{-1} due to an Re=0 stretch which is in the same region as in several well characterized monooxo complexes of rhenium [18, 19]. The UV–Vis spectrum is similar to the spectra of low spin d^2-oxo complexes of rhenium(V) [18].

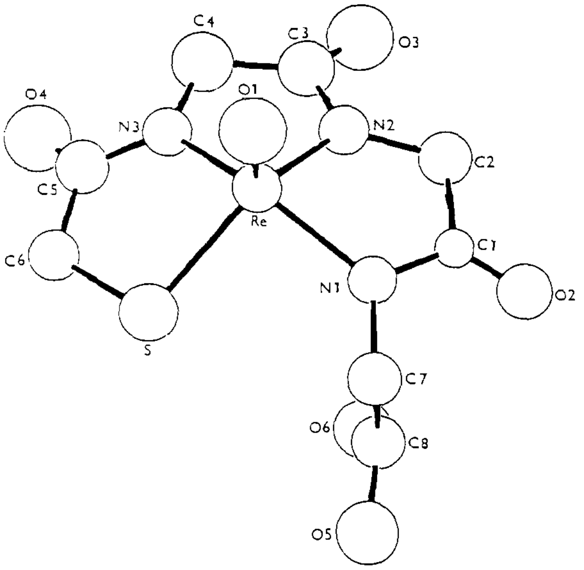

Fig. 2. Perspective view of $Re[C_8H_9O_6N_3S]$ anion. Hydrogen atoms are not shown.

The negative ion FAB-MS shows peaks at 460 and 462 corresponding to the $[Re(C_8H_9O_6N_3S)]^-$ ion. The ^1H NMR spectrum is consistent with the formula $[ReO(MAG_3]^-$.

Figure 2 shows a perspective drawing of $[ReO(MAG_3)]^-$. The fractional coordinates and thermal parameters are presented in Table 1. The bond distances and bond angles of $[ReO(MAG_3)]^-$ are listed in Table 2. The bond distances and bond angles in Bu_4N^+ ion were as expected (see 'Supplementary material'). The crystal structure consists of discrete Bu_4N^+ and $[ReO(MAG_3)]^-$ ions. The geometry around the rhenium atom is square pyramidal with the rhenium atom 0.72 Å away from the basal plane formed by the atoms S(1), N(1), N(2) and N(3). The oxygen atom is at the apex of the square pyramid

TABLE 1. Fractional coordinates ($\times 10^4$, $\times 10^5$ for Re) and U_{eq}/U_{iso} thermal parameters ($Å^2 \times 10^3$) of the non-hydrogen atoms with e.s.d.s in parentheses

	x	y	z	$^*U_{eq}/U_{iso}$[a]
Re	66812(4)	45986(9)	0	39*
S(1)	6657(5)	2655(8)	−780(4)	56(2)
N(1)	6249(12)	5937(23)	−731(11)	42(6)
N(2)	5959(11)	5813(20)	602(11)	35(5)
N(3)	6331(12)	3052(23)	699(11)	45(5)
O(1)	7567(8)	5106(16)	181(9)	59(5)
O(2)	5624(11)	8192(21)	−865(11)	64(5)
O(3)	5278(11)	5893(24)	1624(11)	69(6)
O(4)	6067(12)	688(24)	987(12)	83(6)
O(5)	5015(13)	5008(25)	−1578(11)	74(6)
O(6)	5729(11)	5221(24)	−2556(11)	76(6)
C(1)	5840(13)	7195(25)	−483(13)	31(6)
C(2)	5626(16)	7144(30)	299(14)	53(9)
C(3)	5717(13)	5164(27)	1214(13)	47(6)
C(4)	5977(15)	3621(30)	1350(14)	59(7)
C(5)	6315(16)	1556(32)	562(16)	61(8)
C(6)	6598(15)	1124(29)	−144(14)	64(9)
C(7)	6338(14)	5881(28)	−1522(14)	51(7)
C(8)	5604(14)	5413(30)	−1852(13)	44(6)
N(4)	4066(11)	622(24)	−1679(11)	48(5)
C(11)	3522(17)	−605(36)	−1447(17)	75(9)
C(12)	3809(23)	−1807(47)	−1019(24)	114(13)
C(13)	3209(23)	−3144(45)	−914(22)	106(12)
C(14)	3062(20)	−3985(42)	−1533(20)	95(11)
C(21)	4450(16)	1344(32)	−1071(16)	64(8)
C(22)	3945(18)	2154(37)	−548(17)	75(9)
C(23)	4381(15)	2785(31)	59(38)	86(8)
C(24)	3895(20)	3590(40)	609(20)	91(11)
C(31)	4629(22)	−26(45)	−2221(23)	97(12)
C(32)	5197(24)	1029(52)	−2535(24)	108(14)
C(33)	5659(25)	360(53)	−3078(24)	114(14)
C(34)	6244(37)	−668(78)	−2852(37)	194(26)
C(41)	3581(16)	1791(35)	−2077(16)	68(8)
C(42)	3179(20)	1164(42)	−2742(19)	95(11)
C(43)	2662(18)	2374(38)	−3042(18)	82(9)
C(44)	2272(21)	1899(44)	−3693(21)	98(12)

[a]$U_{eq} = \frac{1}{3}\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$.

TABLE 2. Bond distances (Å) and bond angles (°) of the anion with their e.s.d.s in parentheses

Re–S(1)	2.285(7)	N(3)–C(5)	1.52(4)
Re–N(1)	1.98(2)	C(1)–C(2)	1.52(4)
Re–N(2)	2.04(2)	C(1)–O(2)	1.21(4)
Re–N(3)	2.01(2)	C(3)–C(4)	1.49(4)
Re–O(1)	1.68(1)	C(3)–O(3)	1.28(3)
S(1)–C(6)	1.83(3)	C(5)–C(6)	1.47(4)
N(1)–C(1)	1.43(3)	C(5)–O(4)	1.20(4)
N(1)–C(7)	1.49(3)	C(7)–C(8)	1.51(4)
N(2)–C(2)	1.46(3)	C(8)–O(5)	1.23(3)
N(2)–C(3)	1.36(3)	C(8)–O(6)	1.35(3)
N(3)–C(4)	1.47(3)		
S(1)–Re–O(1)	110.8(6)	Re–N(3)–C(4)	116(2)
S(1)–Re–N(1)	91.1(6)	Re–N(3)–C(5)	125(2)
S(1)–Re–N(2)	139.1(6)	C(4)–N(3)–C(5)	119(2)
S(1)–Re–N(3)	83.0(6)	N(1)–C(1)–C(2)	115(2)
O(1)–Re–N(1)	109.9(8)	N(1)–C(1)–O(2)	124(2)
O(1)–Re–N(2)	109.9(8)	C(2)–C(1)–O(2)	121(2)
O(1)–Re–N(3)	110.5(8)	C(1)–C(2)–N(1)	107(2)
N(1)–Re–N(2)	78.9(8)	N(2)–C(3)–C(4)	117(2)
N(1)–Re–N(3)	138.6(9)	N(2)–C(3)–O(3)	119(2)
N(2)–Re–N(3)	79.4(8)	C(4)–C(3)–O(3)	125(2)
Re–S(1)–C(6)	99.4(9)	C(3)–C(4)–N(3)	109(2)
Re–N(1)–C(1)	117(2)	N(3)–C(5)–C(6)	115(2)
Re–N(1)–C(7)	129(2)	N(3)–C(5)–O(4)	122(3)
C(1)–N(1)–C(7)	114(2)	C(6)–C(5)–O(4)	123(3)
Re–N(2)–C(2)	119(2)	N(1)–C(7)–C(8)	109(2)
Re–N(2)–C(3)	116(2)	C(7)–C(8)–O(5)	131(2)
C(2)–N(2)–C(3)	124(2)	C(7)–C(8)–O(6)	107(2)
		O(5)–C(8)–O(6)	121(2)

with an Re–O bond length of 1.68(1) Å. This distance is at the higher end of the 1.60–1.69 Å range observed for a number of monooxo complexes of rhenium(V) and technetium(V) [20]. The Re–S bond distance is 2.29(1) Å and the average Re–N bond distance is 2.00 ± 0.02 Å. These values compare favorably with an average Re–S bond distance of 2.283 Å and Re–N bond distance of 1.982 Å in the $Re–N_2S_2$ complex with 2,3-bis(mercaptoacetamido)propanoate [8]. These values are also in agreement with several monooxo rhenium(V) complexes containing similar donor atoms [8, 20–24]. The hydroxyl O(6) of the –COOH group is not bound to the metal as in pencillamine complexes [25] or to the metal–oxo group either directly or through hydrogen bonding. Rather, it forms a strong intermolecular hydrogen bond with carbonyl oxygen O(3) in the molecule at symmetry position ($1-x$, $1-y$, $-\frac{1}{2}+z$). The atoms O(6) and O(3) are separated by a distance of 2.5 Å.

In conclusion, rhenium has been shown to form a stable complex with MAG_3 in the oxidation state five. The crystal structure data confirm that the chelating agent forms structurally identical complexes with both technetium [26] and rhenium. Because of the high stability, facile formation of the complexes, MAG_3 and appropriate derivatives are suitable bifunctional chelating agents for the radiolabeling of monoclonal antibodies for the therapy of cancer with $^{186}Re/^{188}Re$.

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