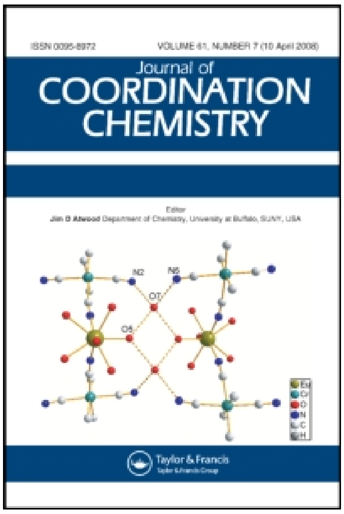

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Gerber, T. I. A. , Luzipo, D. and Mayer, P.(2004) 'Amidobenzoate and carboxylate bonding of 2-amino-3-methylbenzoic acid in an oxorhenium(v) complex', Journal of Coordination Chemistry, 57: 16, 1399 — 1403
To link to this Article: DOI: 10.1080/00958970412331300078
URL: http://dx.doi.org/10.1080/00958970412331300078

J. Coord. Chem., Vol. 57, No. 16, 11 November 2004, pp. 1399–1403

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AMIDOBENZOATE AND CARBOXYLATE BONDING OF 2-AMINO-3-METHYLBENZOIC ACID IN AN OXORHENIUM(V) COMPLEX

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(Received 2 March 2004)

The complex [ReO(Hamb)(H_2amb)(PPh_3)] (**1**) was prepared by the reaction of *cis*-[$ReO_2I(PPh_3)_2$] with two equivalents of 2-amino-3-methylbenzoic acid (H_3amb) in toluene under reflux conditions. Crystallographic data show that **1** contains the coordinated amidobenzoate chelate (Hamb) and symmetrically chelating carboxylate ion (H_2amb) in a pseudo-octahedral geometry.

Keywords: Rhenium; Amidobenzoate; Carboxylate; Anthranilic acid derivative

INTRODUCTION

The current widespread interest in the coordination chemistry of rhenium is mainly due to the potential application of the radioisotopes $^{186/188}$Re in radiotherapy, and its similar chemical behavior to technetium, its second-row congener, which has found major applications in diagnostic nuclear medicine. We have recently described a number of unusual rhenium(V) complexes containing anilines that are substituted in positions 2 and 6 [1–6]. In particular, the reaction of *cis*-[$ReO_2I(PPh_3)_2$] with 3-methyl-2-aminophenol (H_2map) in ethanol led to the formation of *trans*-[Re(map)(Hmap)$I(PPh_3)_2$]I, in which map is only coordinated as a monodentate through the doubly deprotonated amino nitrogen as an imide, and Hmap is present as a bidentate aminophenolate chelate [5]. In addition, with 2-amino-3-methylbenzoic acid (H_3amb) in ethanol, the six-coordinate complex [Re(amb)(OEt)$I(PPh_3)_2$] was isolated, with amb acting as a bidentate chelate via an imido nitrogen and the deprotonated acetoxy oxygen atom [6].

We have now extended this project by repeating the latter reaction in toluene. The complex [ReO(Hamb)(H_2amb)(PPh_3)] (**1**) was isolated as the only product.

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ISSN 0095-8972 print: ISSN 1029-0389 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/00958970412331300078

Hamb is present as a chelating amidobenzoate ligand, with H_2amb being coordinated through a symmetrically chelating carboxylate group with a pendant non-coordinated amino group.

EXPERIMENTAL

cis-[$ReO_2I(PPh_3)_2$] was prepared according to a literature procedure [7] and 2-amino-3-methylbenzoic acid (H_3amb) was purchased from Aldrich. The scientific instrumentation used is the same as reported elsewhere [8]. Infrared spectra were obtained in KBr disks and ^{1}H NMR spectra were run in d_6-DMSO. All reactions and manipulations were carried out in an inert atmosphere.

Synthesis of [ReO(Hamb)(H_2amb)(PPh_3)] (1)

A mixture of 35 mg (232 μmol) of H_3amb and 100 mg (115 μmol) of *cis*-[$ReO_2I(PPh_3)_2$] in 15 cm^3 of toluene was heated under reflux for 60 mins. After heating was stopped and the green solution cooled to room temperature, it was filtered and left to stand at room temperature. After 3 days green platelets were collected by filtration, washed with diethylether, and dried. These crystals, with the formulation **1** · toluene, were suitable for X-ray diffraction studies. Yield 69% (based on Re), mp 156°C. *Anal.* Calcd for $C_{41}H_{38}N_2O_5PRe$(%): C, 57.53; H, 4.47; N, 3.27. Found: C, 57.68; H, 4.41; N, 3.33. IR (KBr, cm^{-1}): $\nu(NH_2)$ 3482, 3457; ν(NH) 3352; $\nu(CO_2^-)$ 1626, 1653; ν(C–O) 1295, 1255; ν(Re=O) 981; ν(Re–N) 507; ν(Re–O) 405, 432. ^{1}H NMR (295 K) ppm: 13.66 (1H, s, NH), 7.89 (1H, d, H(15)), 7.71 (1H, d, H(7)), 7.67 (1H, d, H(13)), 7.32–7.65 (17H, m, PPh_3, NH_2), 7.28 (1H, t, H(14)), 7.19 (1H, d, H(5)), 6.70 (1H, t, H(6)), 2.24 (3H, s, CH_3), 2.18 (3H, s, CH_3).

X-ray Structure Determination

X-ray diffraction studies of crystals of **1** · C_7H_8 were performed at 200(2) K using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo K_α ($\lambda = 0.71073$ Å) radiation. Further details are given in Table I. The structure was solved by direct methods. Nonhydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms bound to carbon were idealized and fixed, with NH and OH protons located by a ΔF map and allowed to refine isotropically. Structural refinements were carried out by the full-matrix least-squares method on F^2 using the program SHELXL-97 [9].

RESULTS AND DISCUSSION

The rhenium(V) complex [ReO(Hamb)(H_2amb)(PPh_3)] (**1**) was synthesized by the reaction of *cis*-[$ReO_2I(PPh_3)_2$] with a twofold molar excess of 2-amino-3-methylbenzoic acid (H_3amb) in toluene, heated under reflux in a nitrogen atmosphere. The purple color of the starting material was replaced by a brown color after 15 min heating, and gradually turned green. When heating was stopped after 1 h, the green solution

TABLE I Crystal data and structure refinement data for **1** · toluene

Empirical formula	$C_{41}H_{38}N_2O_5PRe$
Formula weight	855.94
Temperature (K)	200(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 12.6441(2)$ $b = 18.1210(3)$ $c = 15.9139(3)$ $\beta = 99.0375(8)$
Volume (Å^3)	3601.0(1)
Z	4
Density (calc.) (Mg m^{-3})	1.579
Crystal size (mm)	0.14 × 0.10 × 0.03
F(000)	1712
Absorption coefficient (mm^{-1})	3.467
θ range for data collection (°)	3.2–27.5
Index ranges	$-15 \leq h \leq 16$, $-23 \leq k \leq 23$, $-20 \leq l \leq 20$
Reflections measured	63 198
Independent/observed reflections	8253 ($R_{\text{int}} = 0.109$)/5453 [$I > 2\sigma(I)$]
Data/restraints/parameters	8253/0/455
R, wR_2, S	0.0393, 0.0675, 0.987
Largest diff. peak/hole (e Å^{-3})	1.576/−0.617

deposited green crystals with slow evaporation of the solvent. The reaction is proposed to proceed as follows:

$$[ReO_2I(PPh_3)_2] + 2H_3amb \xrightarrow[\Delta]{} \mathbf{1} + PPh_3 + H_2O + HI.$$

Complex **1** is stable in air and a nonelectrolyte in DMF. It is very soluble in a wide range of solvents such as acetone, methanol, dichloromethane, acetonitrile, DMSO and chloroform.

The dominant feature in the IR spectrum of **1** is the presence of very strong absorption bands at 1626 and 1653 cm^{-1} [$\nu(CO_2^-)$ of Hamb and H_2amb, respectively] and at 981 cm^{-1} [ν(Re=O)]. Peaks of medium intensity at 3482 and 3457 [$\nu(NH_2)$] and at 3352 cm^{-1} [ν(NH)] establish the presence of the free amino group in H_2amb and the amido group in Hamb, respectively. A medium intensity peak at 507 cm^{-1} is assigned to ν(Re–N).

Complex **1** shows sharp, well-resolved peaks in its ^{1}H NMR spectrum. The six-proton signals of the two benzoic acetate rings could easily be assigned, and the signal of the single amido proton lies far downfield at δ13.66 ppm. The two protons of the amino group are obscured by the multiplet of peaks due to PPh_3. The spectrum supports the presence of H_2amb and Hamb in **1**.

The structure of **1** is illustrated in Fig. 1. The rhenium atom is at the center of a pseudo-octahedral environment. The basal plane is defined by the acetoxy oxygens O(3) and O(4), the phosphorus atom and the amido nitrogen N(2). The oxo group O(1) and acetoxy O(2) are in *trans* axial positions.

Selected bond distances and angles are given in Table II. Distortion from an ideal, rhenium-centered octahedron mainly results in a nonlinear O(1)=Re–O(2) axis of 151.9(1)°, with O(4)–Re–P and O(3)–Re–N(2) angles of 162.6(1)° and 154.5(1)°, respectively. The rhenium atom is lifted out of the mean equatorial NO_2P plane by

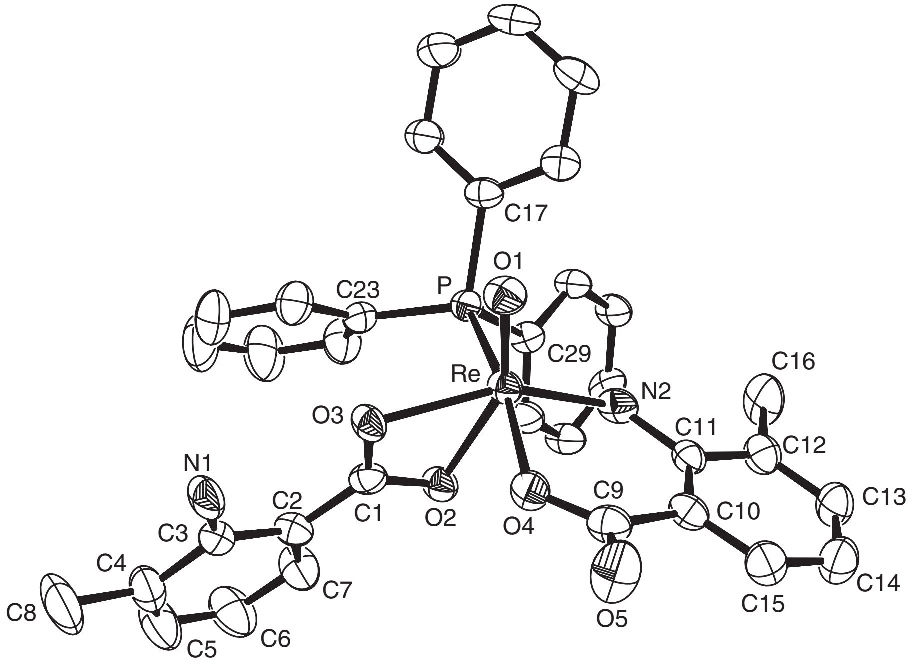

FIGURE 1 An ORTEP view of the structure of **1**, showing the atom labelling scheme and thermal ellipsoids drawn at the 40% probability level.

TABLE II Selected bond lengths (Å) and angles (°) for **1**

Re–O(1)	1.679(3)	Re–O(2)	2.166(3)
Re–P	2.444(1)	Re–N(2)	1.932(4)
Re–O(3)	2.173(3)	Re–O(4)	2.002(3)
C(1)–O(2)	1.287(5)	C(1)–O(3)	1.284(5)
C(9)–O(4)	1.318(5)	C(9)–O(5)	1.228(5)
C(1)–C(2)	1.456(6)	C(3)–N(1)	1.355(6)
C(4)–C(8)	1.504(7)	C(11)–N(2)	1.403(6)
C(12)–C(16)	1.505(6)	C(10)–C(11)	1.402(6)
O(1)–Re–O(2)	151.9(1)	O(2)–Re–O(3)	59.6(1)
O(1)–Re–O(4)	104.8(1)	O(4)–Re–P	162.6(1)
O(1)–Re–N(2)	110.6(2)	N(2)–Re–O(3)	154.5(1)
O(1)–Re–P	92.3(1)	O(2)–C(1)–O(3)	114.0(4)
O(1)–Re–O(3)	94.5(1)	N(2)–C(11)–C(10)	121.9(4)
O(4)–C(9)–O(5)	119.4(4)	C(2)–C(3)–N(1)	122.2(4)

0.383(1) Å toward O(1), as the result of the nonorthogonal angles O(1)–Re–P = 92.3(1)°, O(1)–Re–N(2) = 110.6(2)°, O(1)–Re–O(3) = 94.5(1)° and O(1)–Re–O(4) = 104.8(1)°. Hamb acts as a dianionic bidentate chelate leading to an N(2)–Re–O(4) bite angle of 87.8(1)°. Corresponding Re–N(2)H and Re–O(4) bond lengths are 1.932(4) and 2.002(3) Å, respectively. Re(V)–NH_2 bond distances vary in the range 2.10–2.22 Å [2,10]. The shorter Re–N(2) distance therefore indicates a Re–N(amide) bond. This has also been noted in Re(V) and Tc(V) complexes with amino acids and tetradentate amine oxime ligands [10]. Re–O(4) is slightly below the range that is found (2.074–2.116 Å) for coordinated carboxylate oxygens in positions *cis* to the oxo group in rhenium(V) complexes [11]. The C(9)–O(5) bond length [1.228(5) Å] falls in the range 1.21–1.24 Å observed for this entity in other rhenium(V) complexes. H_2amb binds to rhenium through a *syn* carboxylate anion, with Re–O bond lengths nearly identical, averaging 2.169(3) Å, and an O(2)–Re–O(3) bite angle of 59.6(1)°. A bite angle of 60.12(7)° was observed for the similar coordination of anthranilic acid in $[W(\eta\text{-}C_5Me_5)Cl_3(\eta^2\text{-}O_2CC_6H_4NH_2)]$ [12]. The Re–P distance of 2.444(1) Å is within the range observed (2.41–2.50 Å) for monophosphine oxorhenium(V) complexes. The dihedral angle between the PN(2)O(4)O(3) and ReO(4)C(9)C(10)C(11)N(2) planes is 8.43°, and that between the latter plane and ReO(2)C(1)O(3) is 87.56°.

We believe that complex **1** is novel because it contains both a chelating amidobenzoate and a chelating carboxylate form of the anthranilic acid derivative H_3amb. The amidobenzoate chelate has been observed before in a Mo(VI) complex, while the coordinated carboxylate was found in $[W(\eta\text{-}C_5Me_5)Cl_3(H_2amb)]$ [12].

Supplementary Material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 223505. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; email: deposit@ccdc.cam.ac.uk].

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