

Feature article

Decarboxylation of 5-amino-orotic acid and a Schiff base derivative by rhenium(V)



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ARTICLE INFO

Article history:

Received 30 March 2015

Received in revised form 20 April 2015

Accepted 29 April 2015

Available online 5 May 2015

Keywords:

Decarboxylation

Rhenium(V)

5-Amino-orotic acid

X-ray crystal structures

ABSTRACT

The reaction of 5-amino-orotic acid (H_2aor) with *trans*-[ReOBr₃(PPh₃)₂] in 2-propanol produced the complex [Re^V(apd)Br(aor)(PPh₃)₂] (**1**, apd²⁻ = 5-imidopyrimidine-2,4-dione). The ligand apd²⁻ was formed by the decarboxylation of H_2aor , and it is coordinated via the dinegative imido nitrogen only. The Schiff base derivative of H_2aor , salicylimine-orotic acid {5-(2-hydroxy-benzylideneamino)-1,2,3,6-tetrahydro-2,6-dioxypyrimidine-4-carboxylic acid; H_2sor }, was also decarboxylated in the reaction with *trans*-[ReO₂(OEt)(PPh₃)₂] in ethanol to form [Re^{III}(cor)(PPh₃)₂] (**2**, Hcor = 5-(2-hydroxybenzylideneamino)-pyrimidine-2,4(1H,3H)-dione). Decarboxylation of H_2sor was not observed in its reaction with *trans*-[ReOCl₃(PPh₃)₂], which led to the isolation of [ReOCl(sor)(PPh₃)₂] (**3**), in which sor²⁻ is coordinated as a tridentate ligand as expected. Spectroscopic results and the X-ray crystal structures of compounds **1–3** are also presented.

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Due to its position in Group 7 in the Periodic Table, coupled with the favourable nuclear properties of the ^{186/188}Re nuclides for application in radiotherapy, the metal rhenium has created interest amongst researchers in exploring its coordination chemistry to the extent that the metal has also found application in other areas [1]. The reaction therefore of rhenium with versatile ligands may lead to interesting and unexpected coordination compounds, and to this end we have focussed on 5-amino-orotic acid (2,6-dioxo-5-amino-1,2,3,6-tetrahydropyrimidine-4-carboxylic acid; H_2aor) as a possible ligand for rhenium(V). Metal complexes of orotic acid and its derivatives have been found to display anti-tumour activity [2]. Orotate as a ligand may coordinate to metals via its four oxygen and two nitrogen atoms, leading to a total of 12 different coordination modes in mono- and poly-nuclear complexes [3]. In monomeric complexes, H_2aor can potentially act as a bidentate N,O-donor chelate, either via the carboxylate oxygen and the amino nitrogen (giving a six-membered chelate ring), or via the carboxylate oxygen and pyrimidine nitrogen, giving a five-membered metalocycle.

Research interest in the decarboxylation of organic acids has increased tremendously during the last three decades, mainly because of OMP decarboxylase (ODCase), which is a key enzyme in the biosynthesis of nucleic acids [4].

In the present study we have reacted H_2aor (Fig. 1) with *trans*-[ReOBr₃(PPh₃)₂] [5] in 2-propanol to yield the rhenium(V) complex [Re(apd)Br(aor)(PPh₃)₂] (**1**, Fig. 1; apd²⁻ = 5-imidopyrimidine-2,4-dione) [6]. The X-ray crystal structure shows that the bidentate ligand aor²⁻ is coordinated via the carboxylate oxygen O(113) and

deprotonated pyrimidine nitrogen N(111), with a free amino group N(113)H₂ [7]. However, the monodentate ligand apd²⁻ was formed by the decarboxylation of H_2aor , and is coordinated through the imido nitrogen N(121) only. The Re–N(121) [1.733(3) Å] and Re–N(111) [2.155(3) Å] bond lengths (Table 1) are typical of Re(V)-imido and Re(V)-amido distances respectively [8]. The carboxylate O(113), *trans* to the imido N(121), forms a bond length of 2.049(3) Å to the metal. The two phosphine ligands are coordinated *trans* to each other, with a P(11)–Re–P(12) bond angle of 167.11(4)°. A band of medium intensity in the infra-red spectrum at 1059 cm⁻¹ is ascribed to ν (Re=N) of the coordinated imido-uracil group. The ¹H NMR spectrum is characterized by three singlets in the range 7.08–7.34 ppm and is assigned to the hydrogen atoms on N(123), N(122) and N(112) respectively.

The Schiff base compound H_2sor was synthesized [9] by the condensation reaction of H_2aor and an excess of salicylaldehyde. H_2sor is a potential tridentate O₂N-donor ligand in monomeric complexes. It may coordinate through the phenolate oxygen, imino nitrogen and carboxylate oxygen (giving two 6,6-chelate rings), or via the phenolate oxygen, imino nitrogen and pyrimidyl oxo oxygen, leading to two 6,5-metallorings. The latter coordination scenario would lead to a free uncoordinated carboxylate group. Its reaction with *trans*-[ReO₂(OEt)(PPh₃)₂] in ethanol led to the isolation of the rhenium(III) complex salt [Re(cor)I(PPh₃)₂] (**2**, Fig. 2) [10].

The tridentate ligand cor⁻ was formed by the decarboxylation of H_2sor , and it is coordinated via the deprotonated phenolate O(3), the neutral imino N(3) and the neutral O(1). The O(1)–C(2) and N(3)–C(5) bond lengths are 1.274(4) Å and 1.306(4) Å respectively, and are typical of double bonds [11]. The coordination of a neutral oxygen atom to Re(III) is unusual and rare, and the difference between the

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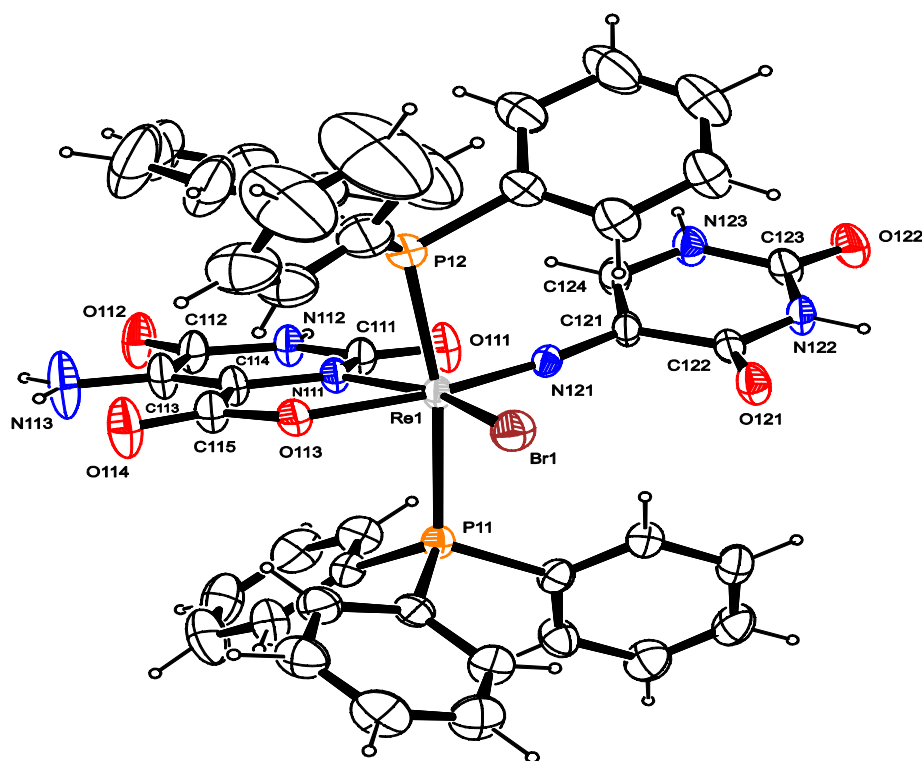


Fig. 1. Crystal structure of **1** with numbered atoms. Ellipsoids are shown at 50% probability level and the solvent 2-propanol and water of crystallization have been omitted for clarity.

Re–O(1) [2.102(2) Å] and Re–O(3) [1.953(2) Å] bond lengths is significant (Table 1). The P(1)–Re–P(2) angle is 177.32(3)°. In the infra-red spectrum two medium intensity peaks at 441 and 459 cm⁻¹ are assigned to $\nu(\text{Re–O}(1))$ and $\nu(\text{Re–O}(3))$ respectively. The ¹H NMR spectrum consists of broad peaks with poor resolution, due to the paramagnetism of the d⁴ complex cation.

Decarboxylation was not observed in the reaction of [ReOCl₃(PPh₃)₂] with H₂SO₄ in ethanol, which led to the formation of the complex [ReOCl(sor)(PPh₃)₂] (**3**, Fig. 3) [12]. The dianionic tridentate sor²⁻ is coordinated via the phenolate O(1), the imino N(1) and carboxylate O (4), with O(1) in the coordination site *trans* to the oxo O(6). The Re–O(6) [1.695(2) Å] distance is typical for an oxo bond to Re(V) [13], and the difference between the Re–O(1) [1.949(2) Å] and Re–O (4) [2.094(2) Å] lengths is significant (Table 1). The N(1)–C (1) bond is double [1.301(5) Å], and the Re–N(1) [2.115(3) Å] is

typical for Re(V)–imine bonds [8]. The typical Re=O stretching frequency occurs at 947 cm⁻¹, and two medium intensity peaks could be assigned for the two Re–O vibrations at 438 and 457 cm⁻¹. The ¹H NMR spectrum is dominated by multiplets of proton signals of the PPh₃ group and phenoxy ring of sor²⁻.

The photochemical decarboxylation of orotic acid to uracil was reported previously [14], and yields of uracil increased if photocatalysis occurs in the presence of Fe(II) or Cu(II) ions and 2-propanol [15].

Table 1
Selected bond lengths [Å] and angles [°] for the complexes **1–3**.

1			
Re–N(121)	1.733(3)	Re–N(111)	2.155(3)
Re–O(113)	2.049(3)	C(113)–N(113)	1.359(6)
N(121)–Re–O(113)	171.8(1)	P(11)–Re–P(12)	167.11(4)
N(11)–Re–O(113)	75.0(1)	Re–N(121)–C(121)	174.1(3)
2			
Re–N(3)	2.071(2)	Re–O(1)	2.102(2)
Re–O(3)	1.953(2)	N(3)–C(5)	1.306(4)
O(1)–Re–O(3)	168.88(8)	P(1)–Re–P(2)	177.32(3)
N(3)–Re–O(1)	79.11(9)	N(3)–Re–O(3)	89.78(9)
C(1)–N(3)–C(5)	121.4(3)	N(3)–Re–I(1)	176.05(7)
3			
Re–O(6)	1.695(2)	Re–O(1)	1.949(2)
Re–O(4)	2.094(2)	Re–N(1)	2.115(3)
N(1)–C(1)	1.301(5)	Re–P(1)	2.4567(9)
O(1)–Re–O(6)	166.6(1)	O(6)–Re–N(1)	89.6(1)
O(6)–Re–O(4)	96.0(1)	N(1)–Re–O(1)	80.9(1)
C(1)–N(1)–C(21)	117.9(3)	Re–O(1)–C(12)	134.7(2)

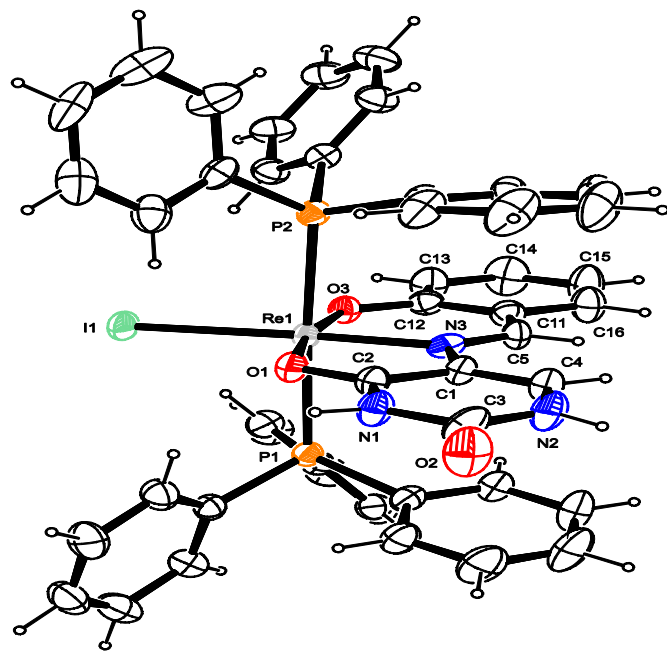


Fig. 2. Crystal structure of **2** with atom numbering. Ellipsoids are shown at 50% probability level and the counter-ion iodide and the solvents ethanol and dichloromethane of crystallization have been omitted for clarity.

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