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Tetraphenylphosphonium [*N*-(2-aminophenyl)-2-(mercaptomethylcarbonylamino)ethanamido-(4−)-κ^4S,N,N',N'']oxorhenate(V)

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The title compound, $(C_{24}H_{20}P)[Re(C_{10}H_9N_3O_2S)O]$, contains well separated square-pyramidal $[ORe L]^-$ complex anions (L is the deprotonated *N*-(2-aminophenyl)-2-(mercaptomethylcarbonylamino)ethanamide ligand) and tetrahedral $[(C_6H_5)_4P]^+$ cations. In the anion, the Re=O bond is oriented along the apical direction and the four basal sites are occupied by one S– and three N-atom donors of the tetradentate L^{4-} ligand.

Comment

With the aim of developing specific technetium and rhenium compounds for eventual application in nuclear medicine, our research group has recently prepared a new family of semi-rigid tetradentate ligands with N_2S_2, ON_2S and N_3S frameworks, and has studied their reactivity with $[TcO]^{3+}$ and $[ReO]^{3+}$ cores (Le Gal *et al.*, 2004, 2005). In a previous paper (Le Gal *et al.*, 2007), we described the structure of the Na⁺ salt of an oxorhenium(V) compound with the N_2S_2 ligand 2-(mercaptomethylcarbonylamino)-*N*-[(2-mercaptophenyl)-ethanamide. A related anionic complex was isolated as the title tetraphenylphosphonium salt, (I), with an N_3S ligand, where the thiol group bonded to the benzene ring has been replaced by an amine. The crystallographic study of this salt was undertaken to confirm the structure proposed from spectroscopic data.

(I)
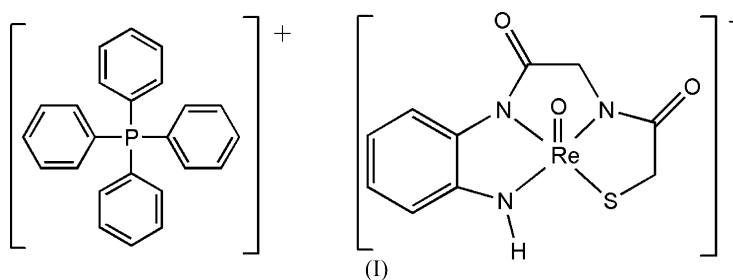
A view of the complex anion of (I) is provided in Fig. 1. The Re atom adopts a square-pyramidal coordination geometry. The axial position is occupied by the oxo ligand, whereas the basal sites are filled by the tetradentate $(NNNS)^{4-}$ ligand. Selected distances and angles are listed in Table 1. The Re=O bond, the Re—S bond and the Re—N bonds to the deprotonated amide atoms N4 and N7 agree with those observed in complexes with the corresponding SNNS ligand (Le Gal *et al.*, 2007) and other tetradentate SNNS or NNNS ligands (Bell *et al.*, 1998; Rao *et al.*, 1990; Hansen *et al.*, 1992; Wong *et al.*, 1997; Lipowska, *et al.*, 2002). The Re—N bond to the terminal deprotonated amine group N1 is significantly shorter than

those observed in similar complexes with mercaptoacetyl-glycylglycylaminobenzoic acids (*ca* 2.021 Å; Hansen *et al.*, 1992); this may be ascribed to the presence of a large aryl substituent on this N donor in the latter case. The Re—N bond is *ca* 0.18 Å shorter than those observed for non-deprotonated amine donors (Wong *et al.*, 1997; Lipowska *et al.*, 2002).

Since the angles between the *trans* bonds are equal [136.81 (10) and 136.79 (7)°], the trigonality index τ is 0.0 (Addison *et al.*, 1984) and the environment of the metal is best described as square-pyramidal. This square pyramid is remarkably regular, the O=Re—(N,S) angles lying in the narrow range 110.27 (10)–111.82 (10)°. The distance from the Re atom to the basal N_3S plane is 0.7503 (12) Å.

The $[(C_6H_5)_4P]^+$ cation shows the expected tetrahedral geometry. Complex anions and $[(C_6H_5)_4P]^+$ cations are packed in the unit cell as well separated entities with normal van der Waals contacts. The terminal N1 donor lies 3.259 (3) Å from the Re=O O atom of an adjacent anion and weak N1—H···O1 hydrogen bonding may be present (geometric details are given in Table 2).

Experimental

Compound (I) was prepared as described earlier (Le Gal *et al.*, 2005). Crystals were obtained by slow evaporation of a solution of the compound in a 1:1 CH_2Cl_2–methanol mixture.

Crystal data

$(C_{24}H_{20}P)[Re(C_{10}H_9N_3O_2S)O]$	$V = 3050.36 (5)$ Å^3
$M_r = 776.83$	$Z = 4$
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation
$a = 10.4122 (1)$ Å	$\mu = 9.25$ mm^{-1}
$b = 29.0410 (3)$ Å	$T = 100 (2)$ K
$c = 10.1031 (1)$ Å	$0.30 \times 0.18 \times 0.09$ mm
$\beta = 93.151 (1)°$	

Data collection

Bruker SMART 2K/PLATFORM diffractometer	24723 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	5969 independent reflections
$T_{min} = 0.168$, $T_{max} = 0.435$	5387 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	388 parameters
$wR(F^2) = 0.068$	H-atom parameters constrained
$S = 1.02$	$\Delta\rho_{max} = 1.41$ e Å^{-3}
5969 reflections	$\Delta\rho_{min} = -0.89$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

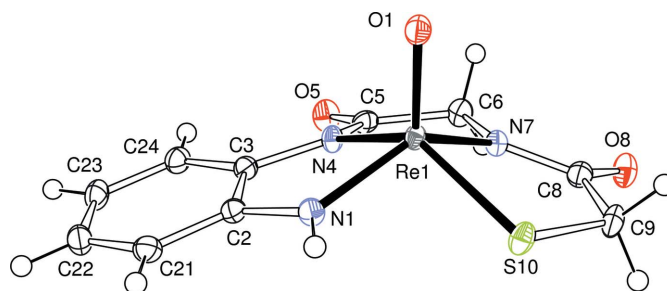|			
Re1—O1	1.706 (2)	Re1—N4	2.013 (2)
Re1—N1	1.968 (2)	Re1—S10	2.2908 (7)
Re1—N7	1.996 (2)		
O1—Re1—N1	110.27 (10)	N4—Re1—N7	78.22 (10)
O1—Re1—N4	111.66 (10)	O1—Re1—S10	111.40 (7)
N1—Re1—N4	77.85 (10)	N1—Re1—S10	90.66 (7)
O1—Re1—N7	111.82 (10)	N7—Re1—S10	82.91 (7)
N1—Re1—N7	136.81 (10)	N4—Re1—S10	136.79 (7)

Figure 1
The structure of the complex anion in (I). Displacement ellipsoids are drawn at the 30% probability level.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^i	0.88	2.40	3.259 (3)	164

Symmetry code: (i) $x, -y + \frac{3}{2}, z - \frac{1}{2}$.

H atoms were positioned geometrically, with C—H = 0.95–0.99 Å and N—H = 0.88 Å, and were included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}$(parent). The maximum residual electron-density peak is located 0.88 Å from atom Re1 and the deepest hole is located 0.82 Å from the same atom. A final check for possible voids was performed using the VOID routine of *PLATON* (Spek, 2003).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *UdMX* (Maris, 2004).

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