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Tetrabutylammonium bis(2-amidobenzenethiolato-κ^2S,N)oxorhenate(V)

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The structure of the title compound, $(C_{16}H_{36}N)[Re(C_6H_5NS)_2O]$, is isomorphous with the corresponding oxotechnetate(V) complex.

Key indicators

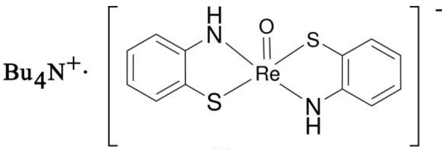
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.013 Å
Disorder in main residue
R factor = 0.053
wR factor = 0.126
Data-to-parameter ratio = 16.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

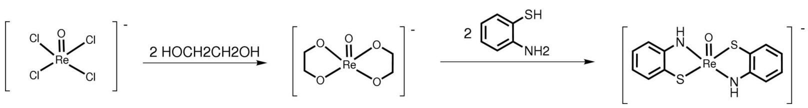
Comment

The coordination chemistry of the dithiolene-like ligand 2-aminobenzenethiol (H_2abt) has been the subject of intensive studies (Gardner *et al.*, 1978; Danopoulos *et al.*, 1990; Herebian *et al.*, 2001; Chaudhuri *et al.*, 2001).

The chemistry of the group VIIb elements technetium and rhenium is of interest to us because their radioactive nuclides are of eminent significance in radiodiagnostics (^{99m}Tc) and radiotherapy (^{186}Re and ^{188}Re). H_2abt forms tris species with these metals, [M(abt)$_3$] (Gardner *et al.*, 1978; Kirmse *et al.*, 1980), as well as bis complexes containing the oxo-metal(V) core [MO(abt)$_2$]$^-$, with the metal in formal oxidation states VI and V, respectively, whereby conversion of the bis complexes into the tris species may be accomplished by treatment of the oxo compound with H_2abt (Bandoli & Gerber, 1987; Spies *et al.*, 1989). The structure of the tris species for both technetium (Baldas *et al.*, 1982) and rhenium (Danopoulos *et al.*, 1990) was confirmed by X-ray diffraction study as being distorted trigonal–prismatic. While the molecular structure of the oxotechnetium(V) complex Bu_4N[TcO(abt)$_2$] was shown to exhibit the square-pyramidal geometry (Bandoli & Gerber, 1987) typical for transition metal complexes of the type [MO(bidentate)$_2$], the structure of the corresponding oxorhenium(V) complex, (I), has not previously been described.



(I)



The preparation of [ReO(abt)$_2$]$^-$ makes use of rhenium(V) precursors, such as rhenium gluconate; a synthetic procedure is given by Noll *et al.* (1996). We describe a modified synthesis (see scheme), based on tetrachlorooxorhenate(V), its conversion into an ethylene glycol complex as an intermediate, and subsequent ligand exchange by H_2abt to form the tetrabutylammonium salt of the abt complex in 62% yield.

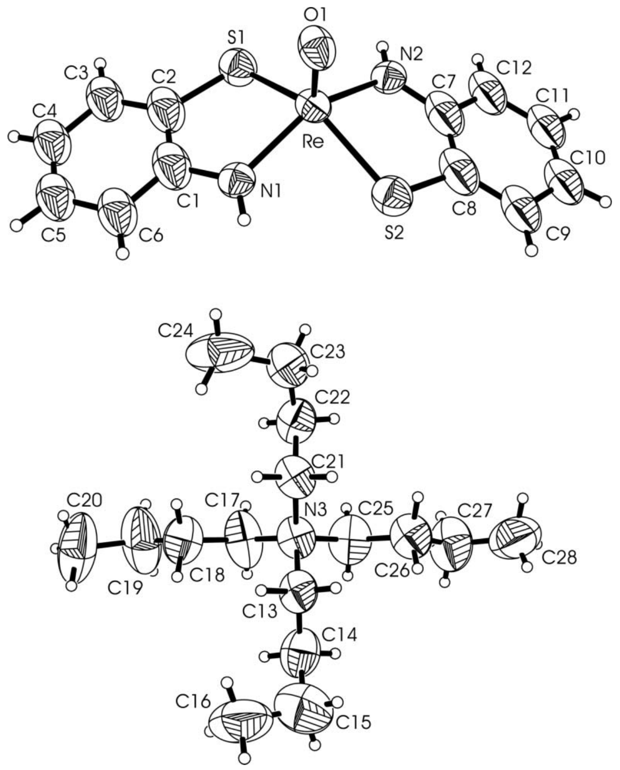


Figure 1
The structure of the $ReO(NHC_6H_4S)_2^-$ anion and Bu_4N^+ cation, showing 30% probability displacement ellipsoids.

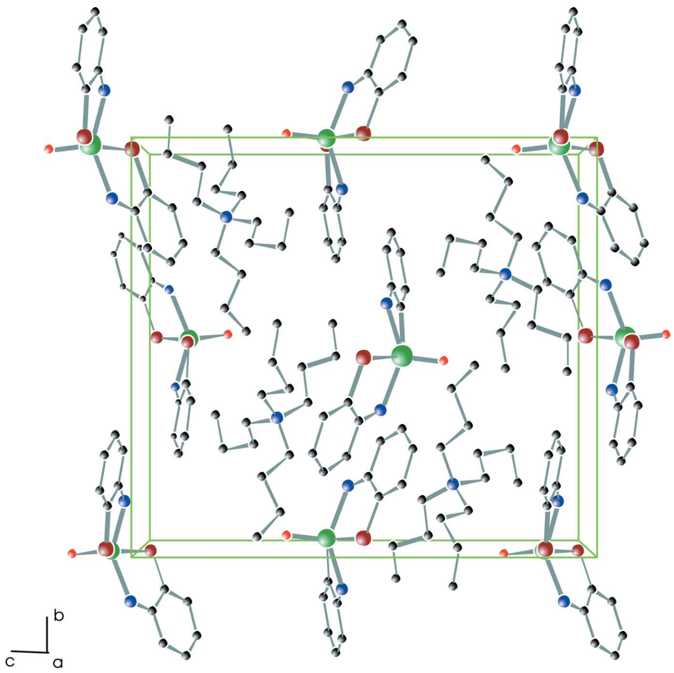


Figure 2
The crystal packing, showing the head-to-tail arrangement of the anions. H atoms have been omitted.

Elemental analysis, and mass, NMR and IR spectra confirm the composition of the title compound as $Bu_4N[ReO(abt)_2]$.

The crystal structure of (I) contains well separated $ReO(NHC_6H_4S)_2^-$ anions and Bu_4N^+ counter-cations. The coordination geometry of Re is distorted square-pyramidal, with an apical Re—O bond length of 1.676 (5) Å. The dihedral angle between the two benzene rings is 33.75 (1)°. These values do not differ much from those of the corresponding Tc compound.

Experimental

The synthesis of $Bu_4N[ReO(abt)_2]$ was carried out as follows. Ethylene glycol (2 ml) was added to a vigorously stirred solution of $Bu_4N[ReOCl_4]$ (100 mg, 0.17 mmol) in methanol (2 ml). The reaction mixture was adjusted to pH ~9 by 1 *M* NaOH and H_2abt (51 mg, 0.41 mmol), dissolved in methanol (1 ml), was added. The colour changed immediately to brown and a solid precipitated. After addition of water (about 1 ml), the mixture was extracted three times with chloroform (each 1 ml). The organic phase was dried with sodium sulfate, filtered and reduced in volume by rotary evaporation. Addition of methanol and further reduction of the volume yielded a red–orange product. Purification by re-crystallization from a cooled acetone–water solution (1:1) (about 258 K) gave the title compound, (I), in 62% yield based on $Bu_4N[ReOCl_4]$ (m.p. 378–380 K). X-ray quality crystals were grown by slow evaporation of a solution in dichloromethane–methanol (1:1). Elemental analysis, calculated for $C_{28}H_{26}N_3OS_2Re$: C 48.7, H 6.7, N 6.1, S 9.3%; found: C 48.7, H 6.7, N 6.0, S 9.4%. Spectroscopic analysis: UV–vis (ethanol, nm): 300 (ε = 24300 M^{-1} cm^{-1}); IR (KBr, cm^{-1}): 933 (Re=O); ^{1}H NMR (400 MHz, $CDCl_3$, δ, p.p.m.): 7.47 (2H, N—H), 6.89–6.54 (8H, C_6H_4), 2.49 (H, N—CH_2), 1.07 (16H, CH_2—CH_2), 0.86 (12H, CH_3). MS (EI) *m*/*z* (%): 448.68 (100) $[ReO(abt)_2]^-$.

Crystal data

$(C_{16}H_{36}N)[Re(C_6H_5NS)_2O]$
$M_r = 691.00$
Orthorhombic, $P2_12_12_1$
$a = 11.821 (5)$ Å
$b = 15.426 (6)$ Å
$c = 17.145 (7)$ Å
$V = 3126 (2)$ Å^3

$Z = 4$
$D_x = 1.468$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 4.04$ mm^{-1}
$T = 293 (2)$ K
Block, dark red
0.5 × 0.45 × 0.38 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.165$, $T_{max} = 0.225$

18480 measured reflections
7067 independent reflections
3328 reflections with $I > 2\sigma(I)$
$R_{int} = 0.072$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.125$
$S = 0.84$
7067 reflections
254 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0642P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 1.11$ e Å^{-3}
$\Delta\rho_{min} = -1.37$ e Å^{-3}
Absolute structure: Flack (1983), with 3108 Friedel pairs
Flack parameter: 0.003 (15)

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Table 1
Selected geometric parameters (Å, °).

Re—O	1.676 (5)	N1—C1	1.390 (9)
Re—N1	2.061 (5)	N2—C7	1.349 (10)
Re—N2	2.164 (5)	N3—C17	1.493 (11)
Re—S1	2.299 (3)	N3—C13	1.509 (12)
Re—S2	2.306 (3)	N3—C25	1.546 (13)
S1—C2	1.718 (10)	N3—C21	1.569 (11)
S2—C8	1.686 (10)		
O—Re—N1	110.6 (3)	C2—S1—Re	102.3 (2)
O—Re—N2	108.3 (3)	C8—S2—Re	103.9 (3)
N1—Re—N2	141.11 (18)	C1—N1—Re	119.0 (4)
O—Re—S1	109.1 (2)	C7—N2—Re	113.6 (4)
N1—Re—S1	81.17 (17)	C17—N3—C13	111.4 (8)
N2—Re—S1	86.99 (17)	C17—N3—C25	105.7 (6)
O—Re—S2	107.6 (2)	C13—N3—C25	110.5 (8)
N1—Re—S2	86.17 (17)	C17—N3—C21	110.5 (8)
N2—Re—S2	81.54 (16)	C13—N3—C21	106.0 (6)
S1—Re—S2	143.24 (10)	C25—N3—C21	112.7 (7)

The N and S atoms of the $ReON_2S_2$ inner core are disordered over two positions in a ratio of 0.128 (4):0.882 (4). The highest peak and deepest hole in the final difference Fourier map are located 0.48 and 1.02 Å from Re, respectively. Because of the poor quality of the crystal, restraints were used to handle the very high displacement parameters of some atoms. The disordered N and S atoms were constrained to occupy the same site and to have the same displacement parameters. All H atoms were positioned geometrically and refined as riding, with C—H = 0.93–0.97 Å and O—H = 0.82 Å, and with $U_{\rm iso}(H) = 1.2U_{\rm eq}$(parent atom) ($1.3U_{\rm eq}$ for OH and methyl groups).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); 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: *SHELXTL*.

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