Absorption correction: empirical ψ scan (North *et al.*, 1968)
$T_{min} = 0.667$, $T_{max} = 0.809$
8406 measured reflections
4721 independent reflections
2936 reflections with $I > 2\sigma(I)$

$h = -18 \rightarrow 17$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 19$
2 standard reflections every 120 reflections intensity decay: 1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.164$
$S = 1.079$
4721 reflections
324 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2 + 10.0714P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

The methyl C13 atom is disordered over two positions and was refined isotropically with half occupancy. No H atoms were included for this group. The major residual features in the final difference map lie close to the Co^{III} atom.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Sheldrick, 1995). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1474). Services for accessing these data are described at the back of the journal.

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Bis[2-(1,3-benzothiazol-2-yl)phenolato-*O*,*N*]chlorooxorhenium(V)–dichloromethane (1/1.5)

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Abstract

The X-ray structure of the title compound, $[Re(C_{13}H_8NOS)_2ClO]\cdot1.5CH_2Cl_2$, shows distorted octahedral coordination geometry around rhenium. Bond lengths and angles are typical of related rhenium and technetium complexes. The average Re—N and Re—O distances are 2.140 (4) and 1.977 (4) Å, respectively. The Re═O and Re—Cl distances are 1.679 (4) and 2.365 (1) Å, respectively.

Comment

Current research in radiopharmacology involves the exploitation of the coordination chemistry of technetium as well as its congener, rhenium, to develop new radiotracers (Clarke & Podbielsky, 1987; Jurrisson *et al.*, 1993). The labelled compounds of the radioisotopes of rhenium (^{186}Re/^{188}Re) have been suggested as radiopharmaceuticals for therapy because of their energetic β particles and accompanying γ rays which are suitable for imaging (Dilworth & Parrotl, 1998). Despite the large number of rhenium complexes discovered thus far, studies of

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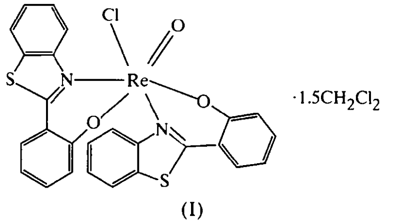
their chemistry and structures are still rare. The present hexacoordinated Re^V complex, (I), is formed from the reaction of rhenium(V) with the bidentate ligand 2-(2-hydroxyphenyl)benzothiazole, which is converted *in situ* from the Schiff base *N*-(2-mercaptophenyl)salicylideneamine (Wilcox *et al.*, 1988; Duatti *et al.*, 1988).



(I)

In the title complex, the Re atom has a distorted octahedral coordination geometry, with the two imine N atoms, one phenolate O atom and one Cl atom in equatorial positions, and the other phenolate O atom and the double-bonded ('yl') O atom in axial positions. The phenolate O atom in the axial position is *trans* with respect to the 'yl' O atom, the two imine N atoms from the two Schiff base ligands are in a *cis* configuration and the two phenolate O atoms are also in a *cis* relationship. The bond lengths and angles are normal and similar to those in a related structure (Wilcox *et al.*, 1988). The steric requirements of the 'yl' O atom severely distort the geometry of the complex and result in non-orthogonal angles at Re (Table 1). As a result, the Re atom is displaced 0.205 Å out of the equatorial plane and towards the 'yl' O atom. This value is similar to those reported for other six-coordinated structures containing the TcO^{3+} core (Wilcox *et al.*, 1988). The Re—N distances of 2.136 (4) and 2.144 (4) Å are slightly longer than those of other reported structures, *e.g.* 2.007 (7) and 2.055 (7) Å in chloro{1,3-[*N*,*N*′-bis(3,5-dichlorosalicylidene)diamino]-2,2-dimethylpropyl}oxorhenium(V), and 2.092 (4) and 2.096 (3) Å in chloro{1,3-[*N*,*N*′-bis(salicylidene)diamino]-2,2-dimethylpropyl}oxorhenium(V) (Herrmann *et al.*, 1996). The Re—Cl distance is 2.365 (1) Å, which is slightly less than those in other reported structures, *e.g.* 2.393 (2) Å in chloro{1,3-[*N*,*N*′-bis(3,5-dichlorosalicylidene)diamino]-2,2-dimethylpropyl}oxorhenium(V) and 2.390 (1) Å in chloro{1,3-[*N*,*N*′-bis(salicylidene)diamino]-2,2-dimethylpropyl}oxorhenium(V). The Re═O distance of 1.679 (4) Å is comparable to the corresponding bond distance of 1.679 (5) Å observed in chloro{1,3-[*N*,*N*′-bis(3,5-dichlorosalicylidene)diamino]-2,2-dimethylpropyl}oxorhenium(V) and 1.680 (3) Å in chloro{1,3-[*N*,*N*′-bis(salicylidene)diamino]-2,2-dimethylpropyl}oxorhenium(V). The $\Delta\rho_{max}$ and $\Delta\rho_{min}$ values are quite large and are located near the Re atom. In one ligand, the angle between the phenyl and benzothiazole rings is 20.7 (3)°, whereas in the other ligand, the angle is 5.6 (3)°. There are one and a half CH_2Cl_2 solvent molecules in the asymmetric unit. One of the two dichloromethane molecules is disordered with 0.5 occupancy. The solvent molecules do not interact with the ligand or with one another.

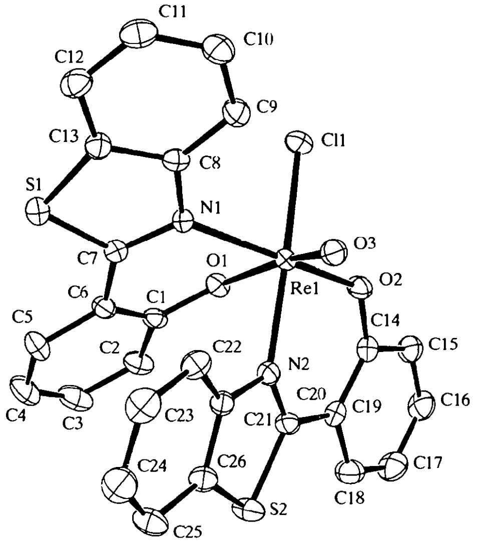


Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids. The solvent and H atoms have been omitted for clarity.

Experimental

The Schiff base ligand was obtained by condensing 2-aminothiophenol with salicylaldehyde (Hill *et al.*, 1979). $Bu_4NReOCl_4$ was synthesized from NH_4ReO_4 following the procedure of Cotton & Lippard (1966). To a dry methanolic solution (10 ml) of the ligand (0.5 mmol, 114 mg), a methanolic solution (15 ml) of $Bu_4NReOCl_4$ (0.5 mmol, 293 mg) was added dropwise. The resulting solution was refluxed for 2 h. An olive-green precipitate was obtained after filtration. The filtrate became brown–red and a red amorphous compound was obtained. Single crystals of the olive-green complex were obtained from dichloromethane solution by slow evaporation over a few days.

Crystal data

$[Re(C_{13}H_8NOS)_2ClO]\cdot 1.5CH_2Cl_2$
M_r = 817.57
Monoclinic
$P2_1/n$
a = 13.320 (2) Å
b = 16.118 (2) Å
c = 13.609 (2) Å
β = 94.76 (1)°
V = 2911.5 (7) Å^3
Z = 4
D_x = 1.865 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 11.18–28.60°
μ = 4.72 mm^{-1}
T = 293 (2) K
Approximately cubic
0.19 × 0.16 × 0.16 mm
Olive green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.40$, $T_{\max} = 0.48$
9084 measured reflections
8455 independent reflections
5456 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.067$
$\theta_{\max} = 29.96°$
$h = -18 \rightarrow 18$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.096$
$S = 0.96$
8455 reflections
379 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.009$
$\Delta\rho_{\max} = 0.87$ e Å^{-3}
$\Delta\rho_{\min} = -1.08$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Re1—O3	1.679 (4)	Re1—Cl1	2.365 (1)
Re1—O2	1.971 (4)	S1—C7	1.726 (5)
Re1—O1	1.984 (3)	S1—C13	1.728 (5)
Re1—N2	2.136 (4)	S2—C26	1.720 (6)
Re1—N1	2.144 (4)	S2—C20	1.732 (5)
O3—Re1—O2	103.6 (2)	O1—Re1—N1	81.3 (1)
O3—Re1—O1	165.0 (2)	N2—Re1—N1	95.0 (2)
O2—Re1—O1	85.0 (1)	O3—Re1—Cl1	101.2 (1)
O3—Re1—N2	86.9 (2)	O2—Re1—Cl1	85.8 (1)
O2—Re1—N2	90.1 (1)	O1—Re1—Cl1	91.5 (1)
O1—Re1—N2	80.8 (1)	N2—Re1—Cl1	171.5 (1)
O3—Re1—N1	91.4 (2)	N1—Re1—Cl1	87.2 (1)
O2—Re1—N1	164.4 (1)		

H atoms were fixed geometrically and refined using constraints with one overall isotropic displacement factor (except for the H atoms of the disordered molecule).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *SHELXL*97.

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(2-Benzoylpyridine-*N* thiosemicarbazonato-N^1,*S*)chloronickel(II)

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Abstract

In the title compound, [Ni($C_{13}H_{11}N_4S$)Cl], the coordination geometry about the Ni^{II} atom is distorted square planar, involving the pyridine N atom, the S atom and the imino N atom from the thiosemicarbazone ligand, and one Cl atom.

Comment

Thiosemicarbazones belong to a large group of thiourea derivatives, the properties of which are functions of the parent aldehyde or ketone (Podhye & Kauffman, 1985; Liberta & West, 1992; Duan *et al.*, 1996). It has been postulated that many N-heterocyclic carbaldehyde thiosemicarbazones act as tridentate ligands with *N*, *N′* and *S* donors, which bond to Fe or Cu in the synthesis of precursors of DNA (West *et al.*, 1993; Liu *et al.*, 1995). Moreover, it has been reported that transition metal complexes of thiosemicarbazones have the potential ability to show second harmonic generation

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