Re—P(1)	2.439 (6)	C(24)—N(2)	1.15 (2)
Re—Cl(1)	2.472 (7)	N(2)—C(25)	1.52 (2)
Re—Cl(3)	2.481 (6)		
C(24)—Re—C(17)	74.2 (11)	P(1)—Re—Cl(3)	157.6 (3)
C(24)—Re—P(2)	109.7 (7)	Cl(1)—Re—Cl(3)	87.8 (2)
C(17)—Re—P(2)	71.2 (8)	C(24)—Re—Cl(2)	78.0 (8)
C(24)—Re—P(1)	110.2 (6)	C(17)—Re—Cl(2)	130.1 (7)
C(17)—Re—P(1)	72.8 (8)	P(2)—Re—Cl(2)	158.5 (2)
P(2)—Re—P(1)	114.7 (3)	P(1)—Re—Cl(2)	79.4 (3)
C(24)—Re—Cl(1)	162.3 (8)	Cl(1)—Re—Cl(2)	88.8 (3)
C(17)—Re—Cl(1)	123.5 (8)	Cl(3)—Re—Cl(2)	83.0 (2)
P(2)—Re—Cl(1)	78.9 (2)	N(1)—C(17)—Re	177 (2)
P(1)—Re—Cl(1)	78.2 (2)	C(17)—N(1)—C(18)	160 (3)
C(24)—Re—Cl(3)	79.0 (7)	N(2)—C(24)—Re	172 (3)
C(17)—Re—Cl(3)	129.5 (8)	C(24)—N(2)—C(25)	160 (3)
P(2)—Re—Cl(3)	79.0 (2)		

Systematic absences: $l = 2n + 1$ in $h0l$; $h + k = 2n + 1$ in $hk0$. Data were corrected for crystal decay and Lp effects. Since our sample suffered extremely fast decay (48% in I by the end of data collection) we collected data using the constant-precision method, prescanning all reflections and not remeasuring those which were found to be 'unobservable' [$I < \sigma(I)$ in prescan]; all reflections for which the counting statistics are obviously poor have therefore been omitted from the final cycles and refinement, in which only 1639 observed data were used. The structure was solved by direct methods (*SIR*92; Altomare, Cascarano, Giacovazzo, Guagliardi, Burla, Polidori & Camalli, 1994) and refined by full-matrix least squares with anisotropic displacement parameters for the Re, P and Cl atoms. H atoms were included at calculated positions and given a common isotropic displacement parameter [refined $U_H = 0.12\,(2)$ Å^2]. One of the cyclohexyl rings was found to be disordered; the two half-occupancy moieties were given a common displacement parameter and had their bond lengths constrained (C—C = 1.54 Å), and H atoms omitted. The 1,2-dichlorobenzene solvent molecule was found to have full occupancy.

Calculations were carried out on a Silicon Graphics Personal Indigo computer, running IRIX 4.01 with *SHELXL*93 (Sheldrick, 1993). Molecular graphics were produced using *ORTEP*II (Johnson, 1971).

We thank the Italian CNR (Progetto Finalizzato Chimica Fine II) for financial support. The technical support by G. Mezza is also acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1095). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435–436.

Ara, I., Fanwick, P. E. & Walton, R. A. (1991). *J. Am. Chem. Soc.* **113**, 1429–1431.

Ara, I., Fanwick, P. E. & Walton, R. A. (1992). *Inorg. Chem.* **31**, 3211–3215.

Bryan, J. C., Stenkamp, R. E., Tulip, T. H. & Mayer, J. M. (1987). *Inorg. Chem.* **26**, 2283–2288.

Che, C. M., Wang, Y. P., Yeung, K. S., Wong, K. Y. & Peng, S. M. (1992). *J. Chem. Soc. Dalton Trans.* pp. 2675–2677.

Drew, M. G. B., Brisdon, B. J. & Watts, A. M. (1984). *Polyhedron*, **3**, 1059–1063.

Drew, M. G. B., Davis, K. M., Edwards, D. A. & Marshalsea, J. (1978). *J Chem. Soc. Dalton Trans.* pp. 1098–1102.

Fletcher, S. R. & Skapski, A. C. (1974). *J. Chem. Soc. Dalton Trans.* pp. 486–489.

Johnson, C. K. (1971). *ORTEP*II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

Jurisson, S., Francesconi, I., Linder, K. E., Treher, E., Malley, M. F., Gougoutas, J. Z. & Nunn, A. D. (1991). *Inorg. Chem.* **30**, 1820–1827.

Leeaphon, M., Fanwick, P. E. & Walton, R. A. (1991). *Inorg. Chem.* **30**, 4986–4995.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.

Treichel, P. M., Williams, J. P., Freeman, W. A. & Gelder, J. I. (1979). *J. Organomet. Chem.* **170**, 247–258.

Warner, S., Cheatham, L. K., Tulip, T. H., Williams, I. D. & Lippard, S. J. (1991). *Inorg. Chem.* **30**, 1221–1226.

Acta Cryst. (1995). C**51**, 203–205

[3,10-Diethyl-5,8-diazadodecane-3,10-dithiolato(3–)-*N*,*N*′,*S*,*S*′]oxorhenium(IV) Chloroform Solvate

TREVOR W. HAMBLEY

School of Chemistry, University of Sydney, NSW 2006, Australia

ROBERT K. KNOTT, TIMOTHY W. JACKSON,
MASAHARU KOJIMA AND RICHARD M. LAMBRECHT

Biomedicine and Health Program, Australian Nuclear Science and Technology Organisation, Private Mail Bag 1, Menai, NSW 2234, Australia

(*Received* 5 *May* 1994; *accepted* 30 *June* 1994)

Abstract

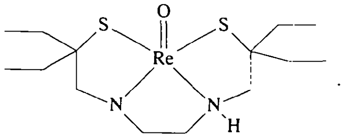
The structural analysis of the title compound $[Re(C_{14}H_{29}N_2S_2)O].CHCl_3$ was undertaken in order to determine whether the high solubility of the complex in chloroform was due to disruption of the hydrogen bonding between complexes. The N—H···O hydrogen-bonding scheme previously observed in the non-solvated material was found to persist in the chloroform solvate. The chloroform molecules occupy hydrophobic pockets created by the ethyl substituents and are involved in close contacts with the coordinated S atoms.

Comment

Rhenium complexes involving radioactive ^{186}Re and ^{188}Re have potential as tumour-targetting radiotherapeu-

Acta Crystallographica Section C
ISSN 0108-2701 ©1995

tic agents. The chemical similarities between technetium and rhenium have prompted us to investigate the Re complexes of ligands that have been used successfully in diagnostic imaging using ^{99m}Tc (Jackson, Kojima & Lambrecht, 1993). Substantial differences have emerged between the properties of the Re and Tc complexes, the most frustrating of which has been the lower water solubility and lipophilicity of the Re complexes. The crystal structure determination of the title complex, [ReO(tedadt)], in the unsolvated form obtained from acetone, revealed that one of the amine groups was deprotonated and that pairs of complexes form strongly hydrogen-bonded dimers (Jackson, Kojima & Lambrecht, 1993). The hydrogen bonding involves the oxo ligand and the remaining amine H atom and probably accounts for the low solubility of the Re complex. The complex was found to have a particularly high solubility in chloroform and crystallization from chloroform gave crystals that shattered on prolonged exposure to air, evidently due to loss of the chloroform solvent. The structure determination of this putative solvate, (I), was undertaken to establish whether the high solubility in chloroform was associated with disruption of the hydrogen-bonded dimers and/or protonation of both amines.



(I)

A view of the title complex in the chloroform solvate form with the atom-numbering scheme is given in Fig. 1. The presence of a chloroform solvate was confirmed by the structure determination, but the geometry about Re, the deprotonation of one amine and the formation of an N—H···O hydrogen-bonded dimer [N···O 2.82 (2), H···O 1.96 Å] were found to be similar to those reported for the solvent-free form of the structure. Accordingly, the structural details of the complex are not discussed further.

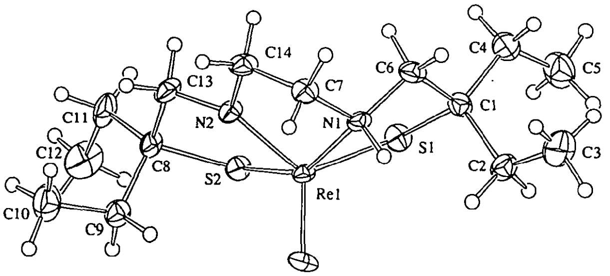


Fig. 1. A view of the title complex in the chloroform solvate form with the atom-numbering scheme. Non-H atoms are shown at the 30% probability level.

The solvated form of the structure crystallizes with the two halves of the dimer related by a centre of symmetry at $0,\frac{1}{2},\frac{1}{2}$. The chloroform molecules occupy pockets surrounded primarily by the ethyl substituents of the ligands (Fig. 2). The H atom of the chloroform molecule is disposed directly towards the two S atoms of one complex with H···S contacts of 2.91 and 2.93 Å. These contacts do not qualify as strong hydrogen bonds but are likely to be energetically favourable. Thus, the high solubility of the complex in chloroform probably arises from a combination of hydrophobic contacts between the solvent and the ethyl groups and weak hydrogen bonds between the chloroform and the S donor atoms.

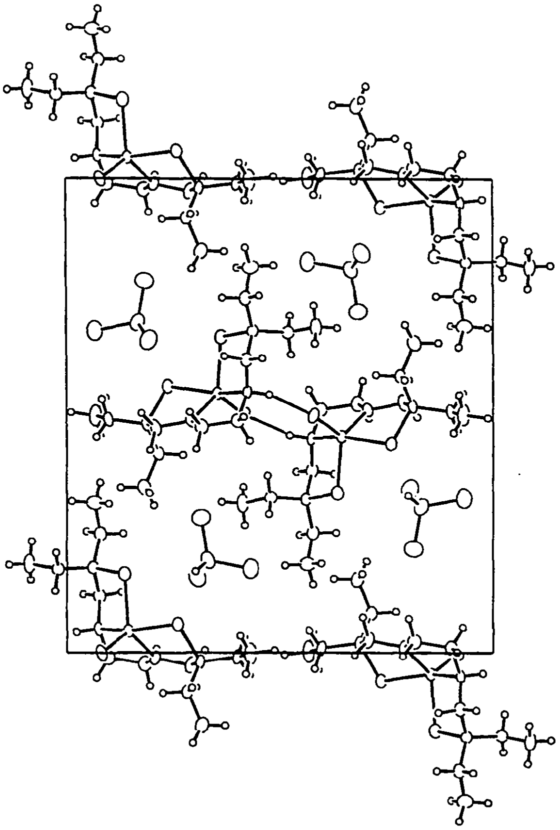


Fig. 2. *ORTEP* (Johnson, 1965) plot of the unit cell showing the chloroform molecules occupying hydrophobic pockets in the lattice, viewed down the *a* axis with the *b* axis vertical and the *c* axis horizontal.

Experimental

Crystals were grown by evaporation from chloroform solution. The crystals were coated with epoxy resin to minimize solvent loss but substantial decomposition still occurred during data collection.

Crystal data

$[Re(C_{14}H_{29}N_2S_2)O].CHCl_3$
$M_r = 611.10$
Monoclinic
$P2_1/n$
$a = 7.058$ (7) Å
$b = 18.962$ (7) Å
$c = 17.05$ (2) Å
$\beta = 90.92$ (9)°
$V = 2281$ (2) Å^3
$Z = 4$
$D_x = 1.779$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7109$ Å
Cell parameters from 25 reflections
$\theta = 9.0–12.0°$
$\mu = 5.867$ mm^{-1}
$T = 273.2$ K
Needle
0.45 × 0.18 × 0.15 mm
Purple

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–θ scans
Absorption correction: analytical
$T_{\min} = 0.252$, $T_{\max} = 0.521$
4301 measured reflections
4031 independent reflections

3307 observed reflections $[I > 2.5\sigma(I)]$
$R_{\rm int} = 0.039$
$\theta_{\max} = 25°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 60 min
intensity decay: −33.37%

Refinement

Refinement on F
$R = 0.0500$
$wR = 0.0540$
$S = 3.530$
3307 reflections
218 parameters
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\max} = 0.011$
$\Delta\rho_{\max} = 3.35$ e Å^{-3}
$\Delta\rho_{\min} = -3.79$ e Å^{-3}

Extinction correction: Zachariasen (1967) type 2, Gaussian isotropic
Extinction coefficient: 0.04708
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Re(1)	0.02523 (6)	0.54556 (3)	0.35493 (3)	0.0288
Cl(1)	0.9208 (6)	0.1569 (3)	0.3060 (3)	0.0840
Cl(2)	0.6621 (7)	0.1754 (3)	0.4324 (3)	0.0896
Cl(3)	0.6935 (7)	0.2822 (3)	0.3151 (3)	0.0921
S(1)	0.0110 (5)	0.6643 (2)	0.3646 (2)	0.0414
S(2)	0.1736 (4)	0.5603 (2)	0.2384 (2)	0.0383
O(1)	0.175 (1)	0.5000 (5)	0.4190 (5)	0.0420
N(1)	−0.228 (1)	0.5500 (5)	0.4250 (5)	0.0315
N(2)	−0.144 (1)	0.4885 (5)	0.2921 (6)	0.0338
C(1)	−0.179 (2)	0.6775 (7)	0.4383 (8)	0.0381
C(2)	−0.089 (2)	0.6741 (7)	0.5208 (8)	0.0474
C(3)	−0.224 (2)	0.6858 (9)	0.5869 (9)	0.0701
C(4)	−0.278 (2)	0.7480 (8)	0.4210 (8)	0.0535
C(5)	−0.158 (3)	0.8137 (8)	0.434 (1)	0.0757
C(6)	−0.322 (2)	0.6180 (7)	0.4232 (8)	0.0394
C(7)	−0.354 (2)	0.4886 (7)	0.4024 (8)	0.0395
C(8)	0.088 (2)	0.4802 (7)	0.1871 (7)	0.0357
C(9)	0.208 (2)	0.4174 (7)	0.2165 (8)	0.0418
C(10)	0.152 (2)	0.3467 (9)	0.1831 (9)	0.0690
C(11)	0.106 (2)	0.4911 (8)	0.0981 (8)	0.0599
C(12)	0.310 (2)	0.4983 (10)	0.0682 (9)	0.0755
C(13)	−0.119 (2)	0.4734 (8)	0.2090 (8)	0.0435
C(14)	−0.340 (2)	0.4760 (7)	0.3162 (8)	0.0429
C(15)	0.702 (2)	0.1930 (8)	0.3321 (9)	0.0583

Table 2. *Selected geometric parameters* (Å, °)

Re(1)—S(1)	2.260 (4)	N(2)—C(14)	1.46 (1)
Re(1)—S(2)	2.278 (4)	C(1)—C(2)	1.54 (2)
Re(1)—O(1)	1.737 (8)	C(1)—C(4)	1.53 (2)
Re(1)—N(1)	2.17 (1)	C(1)—C(6)	1.53 (2)
Re(1)—N(2)	1.93 (1)	C(2)—C(3)	1.51 (2)
Cl(1)—C(15)	1.76 (1)	C(4)—C(5)	1.52 (2)
Cl(2)—C(15)	1.77 (2)	C(7)—C(14)	1.49 (2)
Cl(3)—C(15)	1.72 (2)	C(8)—C(9)	1.54 (2)
S(1)—C(1)	1.87 (1)	C(8)—C(11)	1.54 (2)
S(2)—C(8)	1.85 (1)	C(8)—C(13)	1.52 (2)
N(1)—C(6)	1.45 (1)	C(9)—C(10)	1.51 (2)
N(1)—C(7)	1.51 (2)	C(11)—C(12)	1.54 (2)
N(2)—C(13)	1.46 (2)		
S(1)—Re(1)—S(2)	87.8 (1)	C(2)—C(1)—C(4)	113 (1)
S(1)—Re(1)—O(1)	118.5 (3)	C(2)—C(1)—C(6)	113 (1)
S(1)—Re(1)—N(1)	83.3 (3)	C(4)—C(1)—C(6)	108 (1)
S(1)—Re(1)—N(2)	124.9 (3)	C(1)—C(2)—C(3)	115 (1)
S(2)—Re(1)—O(1)	109.1 (3)	C(1)—C(4)—C(5)	116 (1)
S(2)—Re(1)—N(1)	150.6 (3)	N(1)—C(6)—C(1)	111 (1)
S(2)—Re(1)—N(2)	82.8 (3)	N(1)—C(7)—C(14)	109 (1)
O(1)—Re(1)—N(1)	99.8 (4)	S(2)—C(8)—C(9)	108.0 (9)
O(1)—Re(1)—N(2)	115.9 (4)	S(2)—C(8)—C(11)	109 (1)
N(1)—Re(1)—N(2)	79.5 (4)	S(2)—C(8)—C(13)	105.1 (9)
Re(1)—S(1)—C(1)	102.4 (4)	C(9)—C(8)—C(11)	112 (1)
Re(1)—S(2)—C(8)	99.3 (4)	C(9)—C(8)—C(13)	112 (1)
Re(1)—N(1)—C(6)	113.7 (8)	C(11)—C(8)—C(13)	110 (1)
Re(1)—N(1)—C(7)	108.5 (7)	C(8)—C(9)—C(10)	115 (1)
C(6)—N(1)—C(7)	114.3 (9)	C(8)—C(11)—C(12)	115 (1)
Re(1)—N(2)—C(13)	124.5 (8)	N(2)—C(13)—C(8)	111 (1)
Re(1)—N(2)—C(14)	120.9 (8)	N(2)—C(14)—C(7)	109 (1)
C(13)—N(2)—C(14)	112 (1)	Cl(1)—C(15)—Cl(2)	109.0 (9)
S(1)—C(1)—C(2)	108.5 (9)	Cl(1)—C(15)—Cl(3)	111.6 (8)
S(1)—C(1)—C(4)	108.4 (9)	Cl(2)—C(15)—Cl(3)	110.1 (9)
S(1)—C(1)—C(6)	105.4 (9)		

H atoms were refined riding on their associated C or N atoms with C—H and N—H distances of 0.95 Å.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1012). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Jackson, T. W., Kojima, M. & Lambrecht, R. M. (1993). *Aust. J. Chem.* **46**, 1093–1097.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1993). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Sheldrick, G. M. (1985). *SHELXS*86. In *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford Univ. Press.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.