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Tetrakis(μ-benzothiazole-2-thiolato)-1:2κ^4*N*:*S*^{2};1:2κ^4*S*^{2}:*N*-dichloro-1κ*Cl*,2κ*Cl*-dirhenium(III)(*Re*—*Re*) dichloromethane solvate: a bridged complex with a long Re—Re quadruple bond

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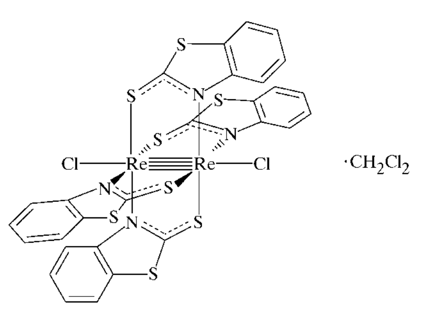
The title compound, $[Re_2(C_7H_4NS_2)_4Cl_2]\cdot CH_2Cl_2$, consists of dirhenium molecules with bridging *N*,*S*-benzothiazole-2-thiolate ligands, axial Cl^- ligands and intramolecular hydrogen bonding. These molecules adopt somewhat staggered conformations, with a long Re—Re quadruple bond distance of 2.2716 (3) Å.

Comment

In the major component, $[Re_2(S_2NC_7H_4)_4Cl_2]$, of the title compound, (I), each of the four benzothiazole-2-thiolate ligands bridges the dirhenium unit by binding through one S atom and the N atom, rather than through both S atoms. The preference of Re^{III} for forming bonds to N rather than S has been documented previously by the discovery of N-bound thiocyanate ligands in the $[Re_2(NCS)_8]^{2-}$ ion (Cotton *et al.*, 1967).



(I)

The four bridging ligands in (I) are arranged so that all N and S atoms are *trans* with respect to each other. This leads to a *cis* arrangement of the N and S atoms around each Re atom. Two axial Cl^- ligands and an Re—Re bond complete the coordination about the dirhenium unit, so that both metal atoms end up in essentially identical pseudo-octahedral environments.

Hydrogen bonding exists between the two Cl^- ligands and the H atoms at the 4-positions on two of the benzothiazole-2-thiolate ligands (Table 2). The Cl1—H24 and Cl2—H3 distances are 2.50 and 2.52 Å, respectively, and these are illustrated by dashed lines in Fig. 1. Apparently, as a result of this hydrogen bonding, the Re—Re—Cl bond angles are bent away from linearity, with values of 158.88 (3) and 159.85 (2)°.

As illustrated in Fig. 2, the molecule takes on a somewhat staggered conformation, with an average torsion angle about the dirhenium axis of 18 (1)°. This torsional twist is far greater than that in any of the compounds with bridging ligands listed in Cotton and Walton's compilation of structural data for

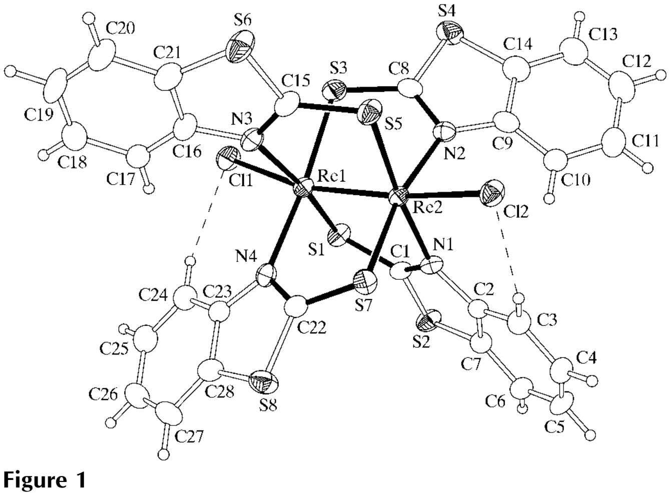


Figure 1
The molecular structure of (I) with 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii and the dichloromethane solvent molecule has been omitted.

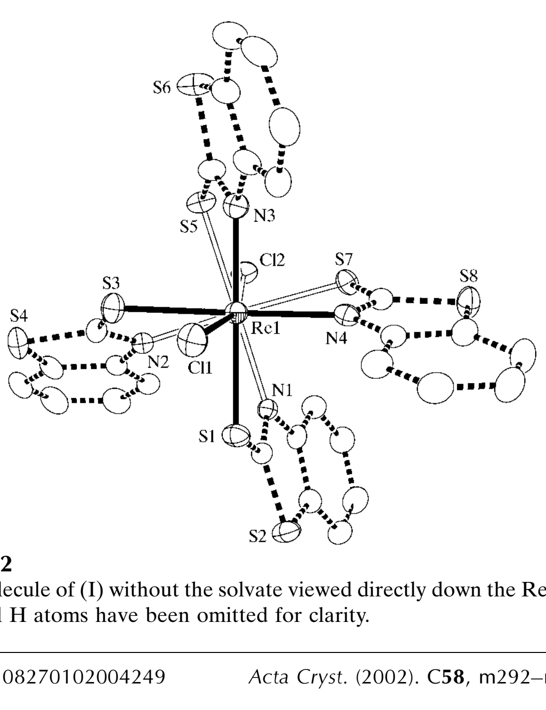


Figure 2
The molecule of (I) without the solvate viewed directly down the Re—Re axis. All H atoms have been omitted for clarity.

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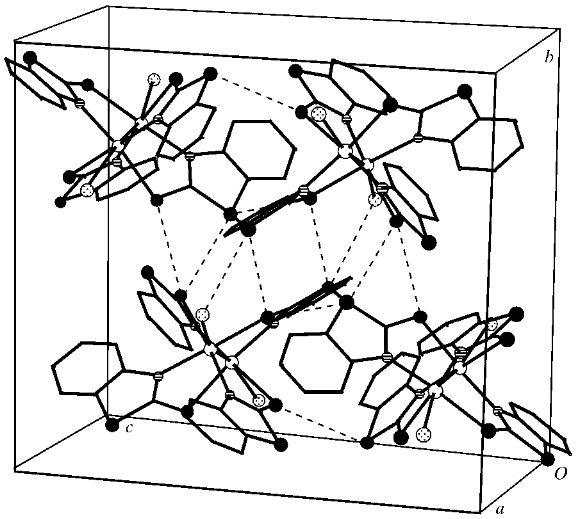

Figure 3
A packing diagram for (I), showing some of the main S···S and S···Cl interactions. Re atoms are indicated by open circles, S atoms by black circles, Cl atoms by speckled circles and N atoms by striped circles.

compounds containing Re—Re quadruple bonds (Cotton & Walton, 1993). The Re—Re bond distance of 2.2716 (3) Å in (I) is also longer than that in any of the bridged compounds in Cotton and Walton's list. Twisting away from an eclipsed conformation is known to weaken the δ component of the quadruple bond (Campbell *et al.*, 1985). However, another factor seems to be at work in (I).

A search of the Cambridge Structural Database (Version 5.22; Allen & Kennard, 1993) for structures published after Cotton and Walton's book went to press has yielded six molecules with Re—Re quadruple bonds longer than 2.25 Å. In each of these molecules, there is at least one bridging ligand. These bridging ligands are 2,6-bis(diphenylphosphino)pyridine (Cotton *et al.*, 1998) and *N*,*N*′-diarylformamidinate, where aryl is *p*-tolyl (Cotton & Ren, 1992), and *p*-methoxyphenyl, 3,4-dichlorophenyl and 3,5-dichlorophenyl (Eglin *et al.*, 1999). All torsion angles about the dirhenium units are less than 12°, but the Re—Re bond distances range from 2.270 to 2.304 Å. This elongation of the quadruple bonds has been attributed to the presence of axial Cl^- ligands (Cotton *et al.*, 1998).

Molecules of (I) pack in a way that maximizes S···S interactions, as shown in Fig. 3. There are intermolecular contacts involving one Cl^- ligand (Cl2) and all the S atoms, with the exception of S4. These non-bonding distances range from 3.467 to 3.626 Å.

Experimental

All synthetic procedures were carried out under a nitrogen atmosphere. Hexachlorobis(methyldiphenylphosphino)dirhenium(III), $Re_2Cl_6(PMePh_2)_2$ (50.1 mg, 0.0508 mmol), 2,2′-dithiobis(benzothiazole) (33.8 mg, 0.102 mmol) and dichloromethane (15 ml) were combined in a 50 ml round-bottomed flask. The mixture was stirred at reflux for 3 h. The resulting deep-purple mixture was filtered through a medium glass frit. Slow evaporation of the filtrate yielded a dark solid. A small amount of this solid was dissolved in dichloromethane (5 ml) and layered with hexanes (20 ml). Thin purple crystals of (I) formed after one week. Analysis calculated for $C_{29}H_{18}Cl_4N_4Re_2S_8$: C 29.19, H 1.52, N 4.70%; found: C 28.54, H 1.66, N 4.79%. IR data (KBr, cm^{-1}): 1608 (*w*), 1465 (*m*), 1353 (*m*), 1322 (*m*), 1288 (*w*), 1253 (*w*), 1109 (*m–s*), 1100 (*vs*), 1047 (*s*), 1026 (*w*), 841 (*m*), 763 (*s*), 754 (*vs*). Visible maxima (nm) in CH_2Cl_2: 742, 620, 539, 427.

Table 1
Selected geometric parameters (Å, °).

Re1—N3	2.100 (3)	Re2—N2	2.103 (3)
Re1—N4	2.159 (3)	Re2—N1	2.139 (3)
Re1—Re2	2.2716 (3)	Re2—S7	2.3786 (9)
Re1—S1	2.3879 (9)	Re2—S5	2.4006 (10)
Re1—S3	2.4126 (10)	Re2—Cl2	2.5529 (10)
Re1—Cl1	2.5488 (11)		
Re2—Re1—Cl1	158.88 (3)	Re1—Re2—Cl2	159.85 (2)
S1—Re1—Re2—N1	−17.44 (8)	N3—Re1—Re2—S5	−17.91 (9)
S3—Re1—Re2—N2	−20.26 (9)	N4—Re1—Re2—S7	−16.46 (8)

Crystal data

$[Re_2(C_7H_4NS_2)_4Cl_2]\cdot CH_2Cl_2$
$M_r = 1193.15$
Monoclinic, $P2_1/c$
$a = 12.9408$ (7) Å
$b = 15.5347$ (8) Å
$c = 17.5303$ (9) Å
$\beta = 92.092$ (1)°
$V = 3521.8$ (3) Å^3
$Z = 4$
$D_x = 2.250$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9504 reflections
$\theta = 2.6$–27.5°
$\mu = 7.68$ mm^{-1}
$T = 213$ (2) K
Plate, purple
0.38 × 0.16 × 0.02 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: analytical face-indexed (*XPREP* in *SHELXTL*; Siemens, 1996)
$T_{min} = 0.174$, $T_{max} = 0.851$
21 991 measured reflections
8000 independent reflections
6368 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 27.5°$
$h = -16 \rightarrow 9$
$k = -20 \rightarrow 18$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.051$
$S = 0.98$
8000 reflections
424 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0185P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.10$ e Å^{-3}
$\Delta\rho_{min} = -0.71$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···Cl2	0.94	2.50	3.347 (4)	150
C24—H24···Cl1	0.94	2.52	3.382 (4)	153

H atoms were treated as riding, with C—H = 0.94–0.98 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The largest peak in the final difference map is located 0.97 Å from solvent atom Cl3.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1996); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1364). Services for accessing these data are described at the back of the journal.

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