Polymorphs and pseudo-polymorphs of μ-oxo-bis{[N,N′-bis(salicylidene)-propane-1,3-diamine]oxorhenium(V)}

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Two new polymorphs of the title compound, μ-oxo-bis{oxo{2,2′-[propane-1,3-diylbis(nitrilomethylidyne)]diphenolato}rhenium(V)}, $[Re_2O(C_{17}H_{16}N_2O_3)_2]$, are reported, containing either a conformation other than the one already known in the literature or a disorder involving both the new and the previously reported conformations. Four pseudo-polymorphs of the title compound are also reported, containing four chloroform, two chloroform, two disordered dichloromethane or two water solvate molecules accompanying each Re complex molecule. Only in the hydrate does the Re complex adopt the old conformation. In all six structures, the complex molecule is located on a crystallographic inversion centre. Independent of the conformation, all ReV ions display the same, somewhat distorted, octahedral coordination. In all the solvates, hydrogen bonds are donated from the solvent to the O atoms bonded to Re, either of the C—H···O or O—H···O type, although the actual position of the solvent molecule can vary. Only in the hydrate is a two-dimensional hydrogen-bonded network found; isolated clusters are formed in all the other solvates.

Comment

μ-Oxo-bis{[N,N′-bis(salicylidene)propane-1,3-diamine]oxorhenium(V)}, (1), [ReO(salpd)]₂O, is readily formed from a number of (alkoxy)- and (aryloxy)[bis(salicylidene)propane-1,3-diamine]oxorhenium(V) compounds, (2), [ReO(salpd)OR] (OR is an alkoxy or aryloxy group), by reacting with water. Presumably, this kind of binuclear Re complex is only formed when the bis(salicylidene)alkanediamine ligand of the starting material has all the coordinating atoms in the equatorial plane of the Re coordination sphere (van Bommel et al.,

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1998). The formation of [ReO(salpd)]₂O involves as the first step the exchange of the alkoxy or aryloxy moiety with water from solvent or air to form [ReO(salpd)OH]. In the second step, two Re–aqua complexes dimerize under elimination of water. We will refer to this process as the dimerization of [ReO(salpd)OR]. Similar reactions have been found for oxorhenium porphyrins (Buchler & Kruppa, 1990) and rhenium dithioether complexes (Reisgys et al., 1997).

We obtained a total of seven crystal structures of polymorphs and pseudo-polymorphs of [ReO(salpd)]₂O during the study of the configurational control of rhenium(V)–bis-(salicylidene)alkanediamine complexes. The crystals were obtained from dimerization reactions in different solvents using a number of different [ReO(salpd)OR] complexes as starting material. In the course of this paper, we will use the term 'modification' to refer to polymorphs, pseudo-polymorphs and solvates. The monoclinic modification of [ReO(salpd)]₂O with Z′ = 1, (I), was recently published by us (van Bommel et al., 1998). We report here the crystallographic details of the other six structures and we will compare the conformation and packing of all seven structures.

(1)
(2)

(II) = (III) = (1)
(IV) = (1)·4CHCl₃
(V) = (1)·2CHCl₃
(VI) = (1)·2CH₂Cl₂
(VII) = (1)·2H₂O

(3)
(4)
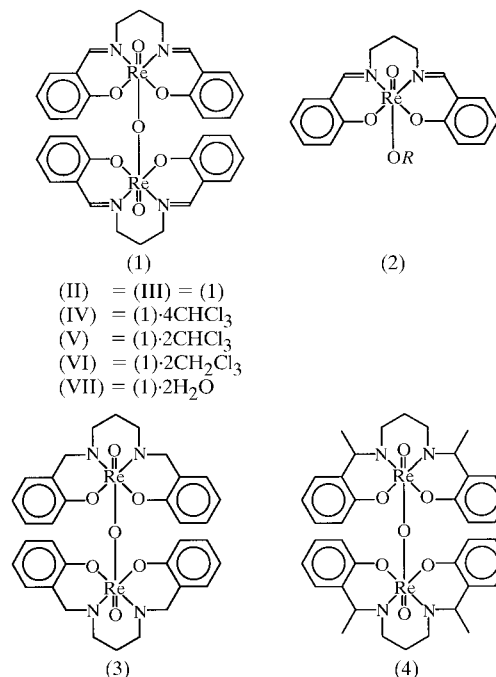
In all structures, the Re complex is located at a crystallographic inversion centre, resulting in a linear central Re—O—Re moiety. This kind of atomic arrangement is often found in similar compounds reported in the Cambridge Structural Database (Allen et al., 1983; version of October 1999). The seven modifications discussed here display no significant differences in bond lengths and angles. The Re—O bond lengths of the central moiety are comparable with those of other chemically symmetric Re—O—Re structures, where Re—O bond lengths are in the range 1.82–1.95 Å. Chemically asymmetric complexes generally have one long (2.0–2.4 Å) and one short (1.75–1.81 Å) bond length. The bis(salicyl-

idene)propanediamine ligands are slightly bent towards the central O atom in all structures; the acute angle between the two phenyl rings of a single bis(salicylidene)propanediamine ligand lies in the range 6.6 (4)–10.4 (5)°. These small angles give rise to deviations from the least-squares plane through all atoms of as much as 0.25 Å.

The Re atom in the seven compounds is six-coordinated; the four donating atoms of the single bis(salicylidene)-propanediamine ligand form the equatorial plane of a somewhat distorted octahedron. Due to the presence of the propane bridge, the N—Re—N angles are slightly larger than the ideal octahedral value [observed range 94.2 (3)–96.8 (5)°], whereas the O_{salpd}—Re—O_{salpd} angles are found to be somewhat smaller than 90° [observed range 80.3 (2)–83.3 (2)°]. The N,O-bite angles tend to be slightly larger than 90° [observed range 90.1 (5)–92.0 (2)°]. The double-bonded O atom is tilted somewhat towards the N atoms of the bis-(salicylidene)propanediamine ligand [N—Re=O angles are in the range 87.6 (6)–90.5 (3)°, whereas O_{salpd}—Re=O are in the range 97.4 (3)–101.0 (2)°]. The bridging O atom is also tilted slightly towards the N atoms. Due to the small displacement of Re out of the coordination plane in the direction of the double-bonded O atom (approximately 0.12–0.15 Å), the angles found for the bridging O atom are smaller then those found for the terminal O atom; N—Re—O_{bridge} angles are in the range 80.4 (2)–85.4 (2)°, whereas O_{salpd}—Re—O_{bridge} are in the range 87.9 (2)–91.5 (2)°.

A more or less similar distortion pattern of the Re coordination was found for μ-oxo-bis{[bis(2-hydroxybenzyl)-propane-1,3-diamine]oxorhenium(V)}, (3), and the 1-(2-hydroxyphenyl)ethyl analogue, (4), which both contain a completely saturated C—N(H)—C—C—C—N(H)—C moiety as the central part of the ligand (Pillai *et al.*, 1994). This similarity is remarkable, since replacement of the C=N bond with a saturated bond can have a great influence on the conformation of the N,O-chelate ring, the conformation of the bis(salicylidene) ligand and the conformation of the dimeric complex as a whole. Whereas the N,O-chelate rings containing a C=N moiety are almost flat, with total puckering amplitudes Q in the range 0.014 (5)–0.147 (5) Å (Cremer & Pople, 1975), the corresponding chelate rings in the saturated systems display values of Q in the range 0.47–0.55 Å. The 1-(2-hydroxyphenyl)ethyl compound adopts a centrosymmetric conformation resembling that of the title compound, whereas the hydroxybenzyl compound is not centrosymmetric and clearly has different conformations for the two ligands. Nevertheless, the N,O-bite angles in both saturated compounds are found to be in the same range as in the [ReO(salpd)]₂O structures reported here.

Modification (I) (van Bommel *et al.*, 1998) was obtained by dimerization of [ReO(salpd)OEt] in ethanol and has two independent half complexes in the asymmetric unit, each located on a crystallographic inversion centre of space group $P2_1/c$. As in the other structures reported in this paper, the bis(salicylidene)propanediamine ligand is slightly bent. All atoms lie more or less within the 'curved plane' of the ligand, with the exception of the central atom of the propane moiety.

In (I), the protruding methylene units of both independent ligands point away from the inversion-related ligand with which the binuclear complex is formed, leaving the six-membered N,N-chelate ring in an envelope conformation. This arrangement of atoms will be referred to as the 'open' conformation throughout this paper, because it allows an unhindered view of the central O atom in a ball and stick model of the complex {the [ReO(salpd)]₂O complex of modification (VII) is also in the open conformation; see Fig. 10}. The conformation is stabilized by intra- and intermolecular C—H···O contacts involving the central CH₂ of the propane moiety and the terminal and salicylidene O atoms (this last only in intermolecular contacts).

Another monoclinic modification, (II), was obtained, which has the same space group as (I), but contains only one unique half Re complex. In this crystal structure, a new conformation was found for the [ReO(salpd)]₂O complex (Fig. 1). The ligands are still slightly curved, but the protruding atom now points towards the inversion-related ligand. This conformation will be called 'closed'. The conformation may be somewhat stabilized by a bifurcated intramolecular C—H···O contact between H9A and both salicylidene O atoms of the inversion-related ligand (Table 2). The complex cannot change to the open conformation without distorting the crystal packing. If neighbouring complexes are not shifted, close contacts would arise between atoms C9 and C5(1 − x, −y, −z) and between atoms H9A and C5(1 − x, −y, −z) (0.47 and 0.83 Å shorter than the sum of the contact radii, respectively). Interestingly, the introduction of the closed conformation in the packing of (I) also results in some unacceptable intermolecular close contacts (more than 0.4 Å shorter than the sum of the van der Waals radii). The packing of modification (II) involves a parallel stacking of the π systems of the C12–C17 ring and its (−x, 1 − y, −z) image [with a symmetry-implied interplane angle of 0° and a Cg···Cg distance of 3.698 (6) Å, where Cg is the geometric centre of the ring]. Apart from the already mentioned C—H···O contacts, the only directional contacts in the packing of (I) are two C—H···π interactions of types N=C—H···π [D···A = 3.716 (8) Å and D—H···A = 117°] and Ph—H···π [involving the H atom *para* to the C=N moiety; D···A = 3.420 (7) Å and D—H···A = 136°].
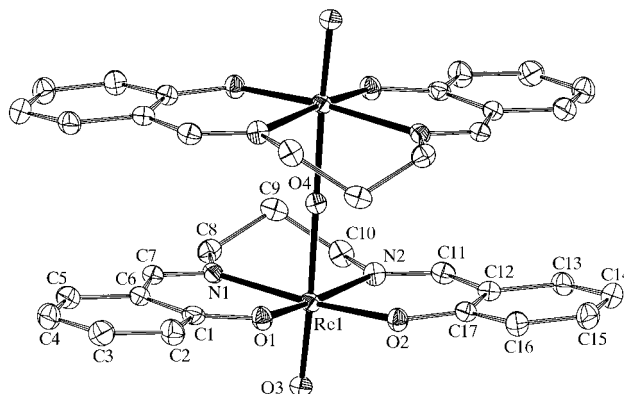

Figure 1
Displacement ellipsoid plot of (II) drawn at the 30% probability level (Spek, 2000). H atoms have been omitted for clarity.
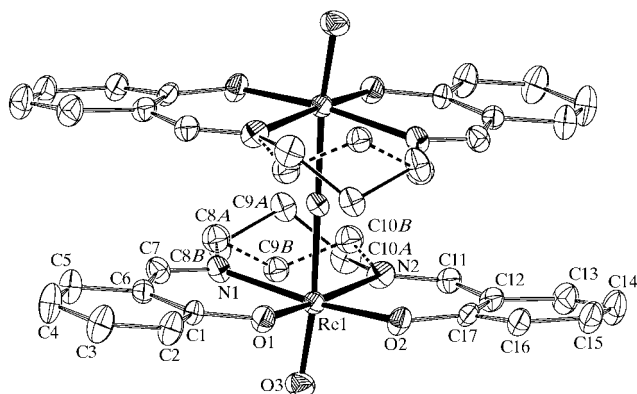
Figure 2
Displacement ellipsoid plot of (III) drawn at the 30% probability level (Spek, 2000). H atoms have been omitted for clarity. Bonds involving atoms of the minor disorder component are dashed.

The orthorhombic modification, (III), was found in the same batch as (II). In (III), both the open and closed conformations occur in a disordered fashion (Fig. 2). The occupancy of the closed conformation was refined to a value of 0.682 (18). The central atom of the propane moiety displays an intramolecular C—H···O contact in both conformations. In the open conformation, the terminal O3 atom is the acceptor, while in the closed conformation one of the salicylidene O atoms (O1) acts as an acceptor (Table 4). The position of the central CH_2 of the propane moiety is therefore slightly different from that found in (II), where the geometry suggests the presence of a symmetric bifurcated hydrogen bond, donating to both O1 and O2, albeit with rather long $D···A$ distances. In both conformations of (III), one of the H atoms of C10 is in a contact position with O3($\frac{1}{2} - x, \frac{1}{2} + y, z$). There are no unfavourable intermolecular short contacts in the major or minor component. Modification (III) does not show $\pi···\pi$ stacking or C—H···π contacts. The fact that we have

now identified crystals containing only the closed conformation, only the open conformation, or a disorder between the open and closed conformations, indicates that the energy difference between the conformations is small. The occupancy observed in (III) and the larger number of structures found which adopt the closed conformation (see below), suggest that the closed conformation has the lowest energy.

Despite differences in intermolecular interaction types (such as $\pi···\pi$ stacking and C—H···π interactions), modifications (I), (II) and (III) all possess layers of molecules in which the geometric centres of the molecules are ordered in an approximate sixfold symmetry. In (II), the layers are arranged so as to mimic a cubic closest packing of spheres (Fig. 3). Each Re complex has contacts with 12 neighbouring molecules. In (III), the layers are shifted somewhat, so a distorted cubic closest packing results. The shift and the orientation of the molecules within one layer enables the contact of two more molecules than in (II) (Fig. 4). In (I), the layers are shifted even more, so that the distribution of geometric centres in layers 1 and 3 is more or less on top of each other, thereby more resembling a hexagonal closest packing than a cubic closest packing. The percentage filled space [calculated according to Kitaigorodskii (1961) using PLATON/VOID (Spek, 2000)] in these modifications shows little variance, with values of 71.7, 70.4 and 72.6% for (I), (II) and (III), respectively.

Modification (IV) is the first in a series of solvent-containing crystal structures of [ReO(salpd)]2O. Two chloroform molecules are found in the asymmetric unit of this monoclinic modification, bringing the ratio Re-complex:-solvent to 1:4. The Re complex adopts the closed conformation. Adoption of the open conformation would give rise to close contacts between H and Cl atoms at an angle unfavourable for possible C—H···Cl interactions. As in the closed conformation in (III), the intramolecular C—H···O contact linking the two ligands in one Re complex involves one of the salicylidene O atoms (Table 6). One of the chloroform solvent
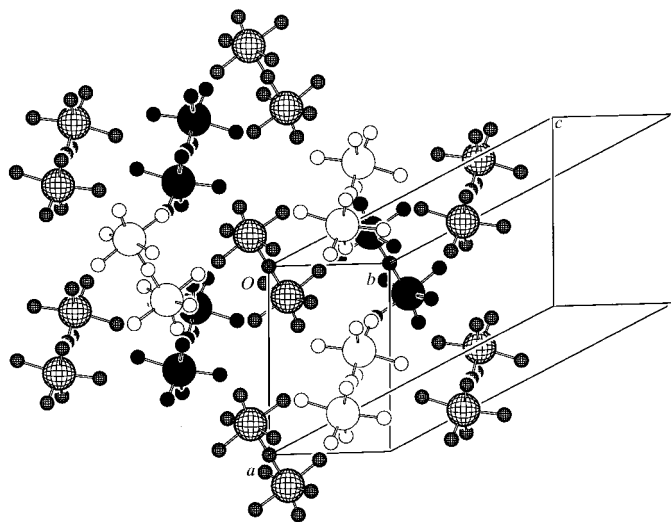

Figure 3
The packing of (II). Only the $Re_2N_4O_7$ core is shown for clarity. Black molecules belong to the bottom layer, hatched molecules belong to the middle layer and white molecules belong to the top layer.
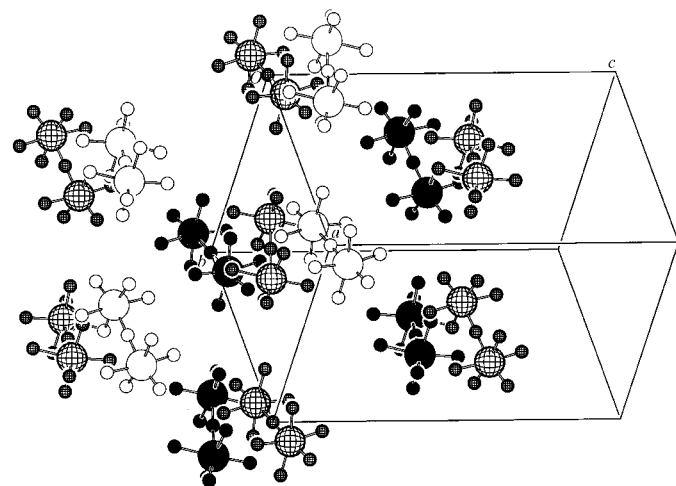

Figure 4
The packing of (III). Only the $Re_2N_4O_7$ core is shown for clarity. Black molecules belong to the bottom layer, hatched molecules belong to the middle layer and white molecules belong to the top layer.
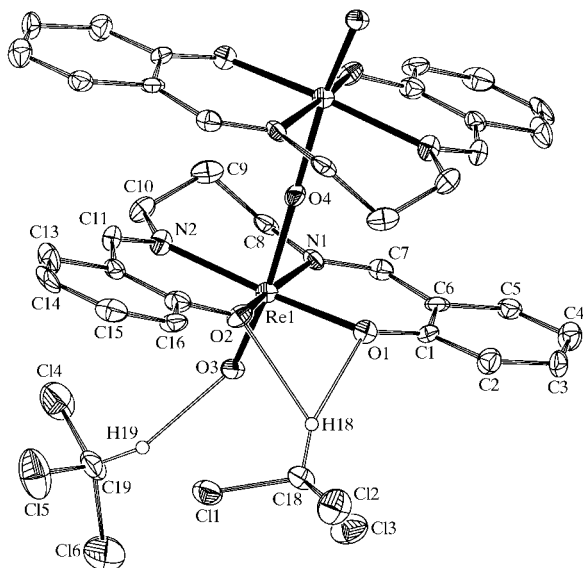
Figure 5
Displacement ellipsoid plot of (IV) drawn at the 30% probability level (Spek, 2000). H atoms are drawn as spheres of arbitrary radii; H atoms not involved in hydrogen bonds have been omitted for clarity

molecules donates a C—H⋯O hydrogen bond to the terminal O atom, while the other chloroform molecule is involved in a symmetric bifurcated hydrogen bond to the salicylidene O atoms (Fig. 5). The crystal packing also shows a number of parallel π-systems, but since the distance between the projection of their geometric centres on one of the ring planes is approximately 3 Å, this system cannot be regarded as a π⋯π stack. The packing clearly differs from the ones observed so far, since in (IV), an Re complex only has contacts with six neighbouring Re complexes instead of 12 [(I) and (II)] or 14 [(III)]. Even if [ReO(salpd)]$_2$O·4CHCl$_3$ is seen as a

single entity, such an entity only displays contacts to ten of its neigbours. A layer structure as found for modifications (I)–(III) can therefore not be identified. Instead, the Re complexes are organized in columns parallel to the *a* axis and are surrounded by a cylindrical layer of chloroform molecules (Fig. 6). The column of Re complexes and solvent molecules is surrounded by six other columns in a hexagonal fashion.

Modification (V) proved to be another chloroform solvate (Fig. 7). In this triclinic modification, only one chloroform molecule is present in the asymmetric unit, resulting in an Re complex–solvent ratio of 1:2. The Re complex is in the closed conformation, with the central CH$_2$ moiety of the propane bridge in contact with one of the salicylidene O atoms of the inversion-related ligand in the same complex. Transformation of the closed conformation to an open conformation without changing the packing would give rise to collisions with one of the phenyl rings of the bis(salicylidene)propanediamine ligand [C9⋯C13(1 − *x*, −*y*, 1 − *z*) would become approximately 0.5 Å shorter than the sum of the van der Waals radii]. The chloroform solvent molecule donates a C—H⋯O hydrogen bond to the O atoms of the Re complex (Table 8). The *D*⋯*A* distance involving the terminal O3 atom is much longer than those involving the salicylidene atoms, O1 and O2. Since the C—H vector of the solvent molecule (which was set equal to the appropriately scaled sum of the three Cl—C vectors) is directed towards O1 and O2 with a small tilt towards O3, we prefer to describe this system as a trifurcated hydrogen bond. The packing of (V) further contains parallel π-systems (ring C1–C6 and its inversion-related image), of which, as in (IV), the geometric centres are too far apart to be regarded as π-stacks. The packing consists of layers of Re complexes, parallel to the *ab* plane, alternated with layers of chloroform (Fig. 8). A layer of Re complexes is ordered along a nearly perfect orthogonal grid, in which each molecule, due to its elongated shape, makes contact with six of its neighbours within the
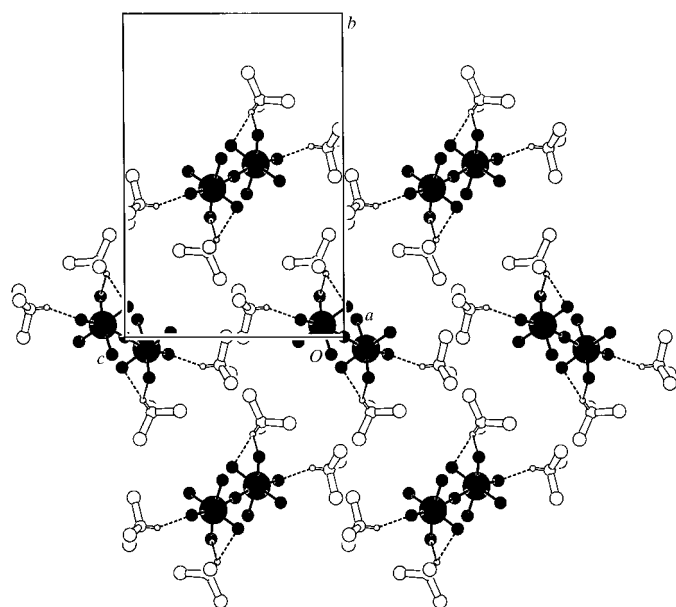

Figure 6
The packing of (IV). Only the Re$_2$N$_4$O$_7$ core (black) and the chloroform molecules (white) are shown for clarity.

Figure 7
Displacement ellipsoid plot of (V) drawn at the 30% probability level (Spek, 2000). H atoms are drawn as spheres of arbitrary radii, H atoms not involved in hydrogen bonds have been omitted for clarity.
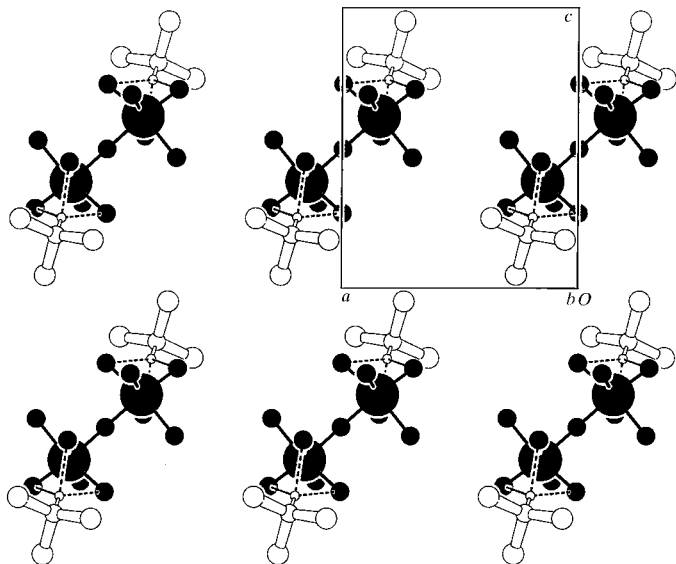
Figure 8
The packing of (V). Only the $Re_2N_4O_7$ core (black) and the chloroform molecules (white) are shown for clarity.

layer. The chloroform layers do not completely separate the Re layers, so that an Re complex in one layer still has contacts with a complex belonging to the next Re layer. The percentage filled space in (V) is 69.6%, slightly higher than the value of 67.5% found for the other chloroform solvate, (IV), but both values are lower than the solvent-free modifications.

The dichloromethane solvate, modification (VI), also contains one solvent molecule per triclinic asymmetric unit (see Fig. 9). Like both chloroform solvates, (VI) shows the Re complex in the closed conformation. The central CH_2 moiety
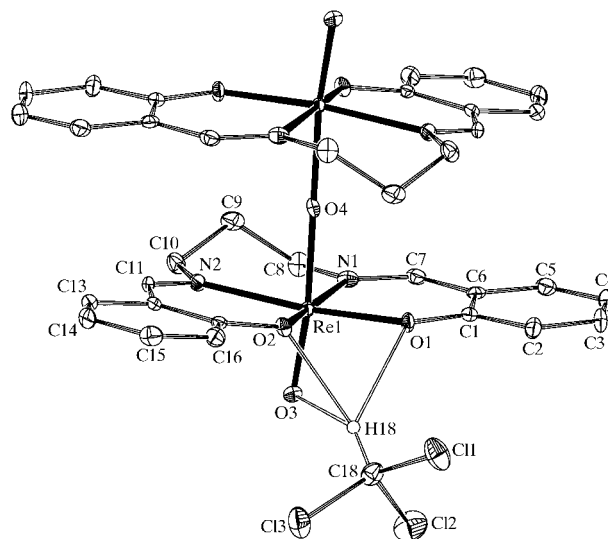

Figure 9
Displacement ellipsoid plot of (VI) drawn at the 30% probability level (Spek, 2000). H atoms are drawn as spheres of arbitrary radii; H atoms not involved in hydrogen bonds have been omitted for clarity. Bonds and hydrogen bonds involving atoms of the minor disorder component are dashed.
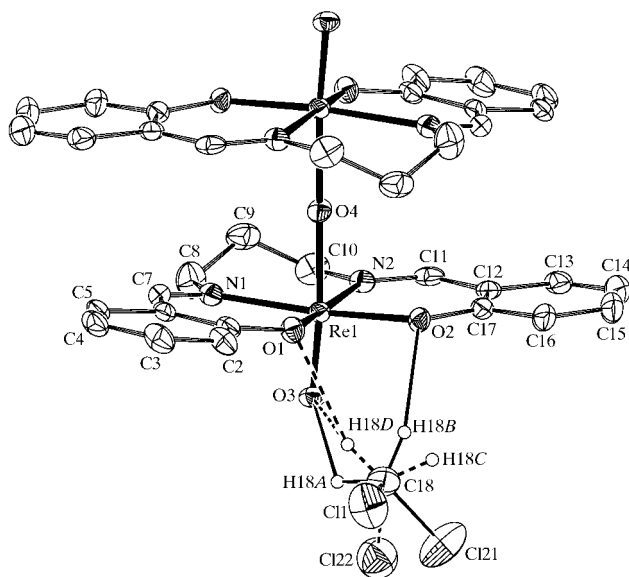
makes a bifurcated C—H···O contact with both salicylidene O atoms, albeit with slightly longer contact distances than in the other closed conformations. The open conformation is again hindered by collisions with one of the phenyl rings of the bis(salicylidene)propanediamine ligand [C9···C13$(1 - x, -y, 1 - z)$ would become approximately 0.3 Å shorter than the sum of the van der Waals radii]. The solvent molecule is disordered over two orientations. The central C atom and one of the Cl atoms occupy the same place in both disordered components; the other Cl atom and the H atoms of the major and minor components are related by a rotation of 46° about the common Cl—C bond. The occupancy of the major component refined to a value of 0.659 (8). Due to the rotation of the H atoms, the major and minor components of the dichloromethane solvate display different hydrogen-bonding schemes. In the major component, both H atoms of the dichloromethane form a hydrogen bond, one to one of the salicylidene O atoms (O2) and one to the terminal O3 atom. In the minor component, only one of the H atoms is involved in hydrogen bonding; it donates a bifurcated hydrogen bond to the other salicylidene O atom (O1) and to the terminal O3 atom. The crystal packing is very similar to that found for (V); in the chosen setting, the layers are oriented parallel to the *ac* plane. One of the differences is that an Re complex makes contact with two Re complexes of the adjacent layer instead of one. The total number of neighbouring molecules in contact with an Re complex is therefore ten. There is a $\pi \cdots \pi$ stack between ring C1–C6 and its $(-x, 1 - y, -z)$ image [with a symmetry-implied interplanar angle of 0° and a $Cg \cdots Cg$ distance of 3.726 (8) Å]. Due to slight shifts in the layer structure, this interaction is severely distorted in the otherwise very similar packing of (V). This indicates that the potential formation of the $\pi \cdots \pi$ stack is not a driving force in the crystal assembly of (V) and (VI). The percentage filled space of the dichloromethane solvate (71.6%) is higher than that of the chloroform solvates.

The last modification, (VII), contained water, which was present in minute quantities in the solvent. The asymmetric unit of this monoclinic modification contains one water mol-
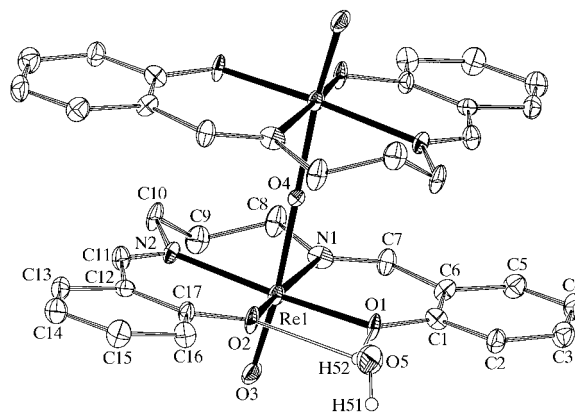

Figure 10
Displacement ellipsoid plot of (VII) drawn at the 30% probability level (Spek, 2000). H atoms are drawn as spheres of arbitrary radii; H atoms not involved in hydrogen bonds have been omitted for clarity.

ecule, bringing the Re complex–solvent ratio to 1:2. In contrast to the other solvates, this Re complex adopts the open conformation; the closed conformation cannot be adopted due to collisions with the hydrate water molecule. Intermolecular O···O distances show that the water molecule joins two Re complexes by donating a bifurcated hydrogen bond with one of its H atoms to the salicylidene atoms O1 and O2 in the same asymmetric unit, and a single hydrogen bond with its other H atom to the terminal O3 atom of the residue at $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$. The location of the Re complexes on a crystallographic inversion centre, combined with the hydrogen bonding, results in the formation of an infinite two-dimensional hydrogen-bonded aggregate with base vectors (0, 1, 0) and (0, 0, 1) (Fig. 11). The $D···A$ distances for the O—H···O hydrogen bonds are somewhat longer than usual. Due to the bulkiness of the Re complex, the water molecule cannot simultaneously approach all the acceptor atoms more closely. Despite the long $D···A$ distances, the packing of the crystal is still the most efficient of all modifications reported here, with a percentage filled space of 73.8%. The crystal packing strongly resembles that found for (III) (Fig. 4), despite the difference in space group. As in (III), the Re complexes are gathered in layers, each of which is ordered in a hexagonal fashion, and a single Re complex makes contact with 14 other Re complexes.

The differences between modifications (VI) and (VII) are interesting, since both solvent molecules possess two hydrogen-bond donors but display different packings. If the water molecule of the hydrate, (VII), had taken a similar position to that of the solvent molecule in (VI), a similar pattern could have been formed with one bifurcated and one single hydrogen bond, both somewhat shorter in length and of approximately equal linearity, as observed in the packing of the hydrate, (VII). In the alternative packing, the Re complex could have adopted the energetically more favourable closed conformation, which is blocked by the presence of the water molecule in the observed packing of the hydrate. Apparently,
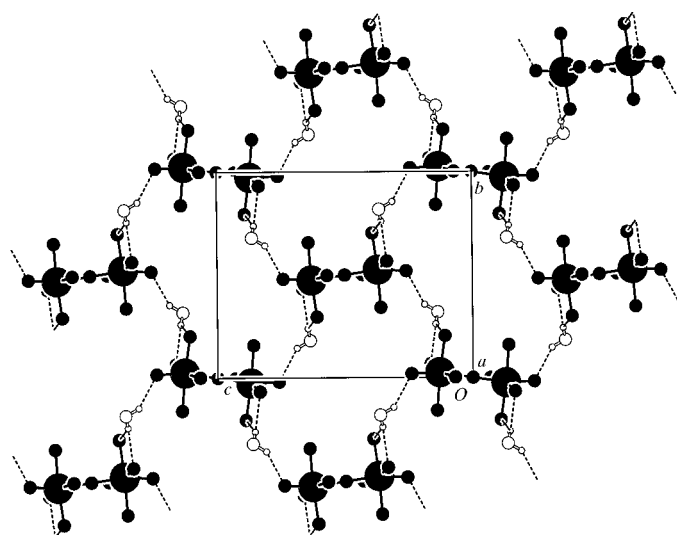
the large void (approximately 95 Å^3, i.e. 10% of the unit cell of the dichloromethane solvate) which would arise if the dichloromethane molecules were replaced by water molecules cannot be filled by adapting the translation symmetry and maintaining a favourable packing at the same time. Another unfavourable factor for the alternative hydrate packing might be that in optimizing the hydrogen-bond geometry, the Re···O distance tends to become smaller than the sum of the contact radii.

The common factor in all four solvates is the presence of hydrogen bonds donated from the solvent to the Re-bonded O atoms. These hydrogen bonds are found in all the different packings, with different positions of the solvent molecules, and for both conformations of the Re complex.

Experimental

Compound (II)

Crystal data

[Re$_2$O(C$_{17}$H$_{16}$N$_2$O$_3$)$_2$]	D_x = 2.069 Mg m^{-3}
M_r = 981.06	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 919
a = 9.044 (3) Å	reflections
b = 10.665 (2) Å	θ = 2.0–20.0°
c = 17.879 (5) Å	μ = 7.74 mm^{-1}
β = 114.07 (5)°	T = 150 K
V = 1574.6 (10) Å^3	Block, dark green
Z = 2	0.40 × 0.30 × 0.25 mm

Data collection

Nonius KappaCCD diffractometer	2582 reflections with $I > 2\sigma(I)$
Area-detector φ and ω scans	R_{int} = 0.104
Absorption correction: multi-scan	θ_{max} = 25.25°
(PLATON; Spek, 2000)	$h = -10 \rightarrow 10$
T_{min} = 0.061, T_{max} = 0.144	$k = -12 \rightarrow 12$
20 915 measured reflections	$l = -21 \rightarrow 21$
2849 independent reflections	

Table 1
Selected geometric parameters (Å, °) for (II).

Re1—O1	2.010 (3)	Re1—O4	1.9152 (7)
Re1—O2	2.016 (4)	Re1—N1	2.118 (5)
Re1—O3	1.712 (4)	Re1—N2	2.125 (5)
O1—Re1—O2	81.61 (15)	O2—Re1—N2	91.02 (17)
O1—Re1—O3	99.26 (16)	O3—Re1—O4	168.63 (12)
O1—Re1—O4	89.40 (12)	O3—Re1—N1	89.12 (18)
O1—Re1—N1	91.11 (17)	O3—Re1—N2	89.07 (18)
O1—Re1—N2	169.62 (18)	O4—Re1—N1	83.33 (14)
O2—Re1—O3	99.02 (16)	O4—Re1—N2	83.19 (14)
O2—Re1—O4	89.47 (12)	N1—Re1—N2	95.23 (19)
O2—Re1—N1	169.83 (17)		

Figure 11
The packing of (VII). Only the Re$_2$N$_4$O$_7$ core (black) and the water molecules (white) are shown for clarity.

Refinement

Refinement on F^2
$R(F) = 0.032$
$wR(F^2) = 0.077$
$S = 1.075$
2849 reflections
214 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 3.0019P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.96$ e Å^{-3}
$\Delta\rho_{min} = -2.96$ e Å^{-3}

Table 2
Hydrogen-bonding and C—H$\cdots$O contact geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C3—H3$\cdots$O2^i	0.95	2.57	3.279 (8)	132
C7—H7$\cdots$O3^{ii}	0.95	2.55	3.161 (8)	122
C9—H9$A\cdots$O1^{iii}	0.99	2.54	3.432 (8)	150
C9—H9$A\cdots$O2^{iii}	0.99	2.56	3.436 (7)	148
C14—H14$\cdots$O3^{iv}	0.95	2.56	3.243 (7)	129

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $1 - x, -y, -z$; (iii) $-x, -y, -z$; (iv) $-x, 1 - y, -z$.

Compound (III)

Crystal data

$[Re_2O(C_{17}H_{16}N_2O_3)_2]$
$M_r = 981.06$
Orthorhombic, $Pbca$
$a = 12.634$ (3) Å
$b = 12.832$ (3) Å
$c = 19.406$ (4) Å
$V = 3146.1$ (12) Å^3
$Z = 4$
$D_x = 2.071$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 830
  reflections
$\theta = 1.6$–$25.0°$
$\mu = 7.75$ mm^{-1}
$T = 150$ K
Irregular needle, dark green
$0.3 \times 0.1 \times 0.1$ mm

Data collection

Nonius KappaCCD diffractometer
Area-detector φ and ω scans
Absorption correction: multi-scan
  (*PLATON*; Spek, 2000)
  $T_{min} = 0.325$, $T_{max} = 0.461$
22 613 measured reflections
2846 independent reflections

2475 reflections with $I > 2\sigma(I)$
$R_{int} = 0.099$
$\theta_{max} = 25.26°$
$h = -11 \rightarrow 15$
$k = -15 \rightarrow 14$
$l = -23 \rightarrow 22$

Table 3
Selected geometric parameters (Å, °) for (III).

Re1—O1	2.035 (7)	Re1—O4	1.9130 (6)
Re1—O2	2.012 (8)	Re1—N1	2.120 (8)
Re1—O3	1.694 (8)	Re1—N2	2.171 (8)
O1—Re1—O2	81.1 (3)	O2—Re1—N2	91.5 (3)
O1—Re1—O3	97.4 (3)	O3—Re1—O4	168.5 (3)
O1—Re1—O4	87.9 (2)	O3—Re1—N1	88.5 (4)
O1—Re1—N1	91.8 (3)	O3—Re1—N2	90.5 (3)
O1—Re1—N2	170.0 (3)	O4—Re1—N1	81.2 (2)
O2—Re1—O3	100.9 (3)	O4—Re1—N2	85.4 (2)
O2—Re1—O4	89.9 (2)	N1—Re1—N2	94.5 (3)
O2—Re1—N1	168.8 (3)		

Table 4
Hydrogen-bonding and C—H$\cdots$O contact geometry (Å, °) for (III).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C9A—H9$B\cdots$O1^i	0.99	2.45	3.386 (16)	158
C10A—H10$B\cdots$O3^{ii}	0.99	2.53	3.469 (17)	157
C10B—H10$C\cdots$O3^{ii}	0.99	2.52	3.49 (4)	163
C11—H11$\cdots$O1^{ii}	0.95	2.56	3.127 (12)	119

Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, z$.

Refinement

Refinement on F^2
$R(F) = 0.048$
$wR(F^2) = 0.112$
$S = 1.217$
2846 reflections
224 parameters

H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.01P)^2 + 50P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.53$ e Å^{-3}
$\Delta\rho_{min} = -3.73$ e Å^{-3}

Compound (IV)

Crystal data

$[Re_2O(C_{17}H_{16}N_2O_3)_2]\cdot4CHCl_3$
$M_r = 1458.53$
Monoclinic, $P2_1/c$
$a = 10.137$ (10) Å
$b = 18.733$ (15) Å
$c = 16.131$ (11) Å
$\beta = 126.43$ (6)°
$V = 2465$ (4) Å^3
$Z = 2$

$D_x = 1.965$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 22
  reflections
$\theta = 9.81$–$13.66°$
$\mu = 5.61$ mm^{-1}
$T = 150$ K
Irregular plate, dark green
$0.5 \times 0.4 \times 0.1$ mm

Data collection

Enraf–Nonius CAD-4T diffract-
  ometer
ω scans
Absorption correction: refined from
  ΔF (*PLATON*; Spek, 2000)
  $T_{min} = 0.138$, $T_{max} = 0.571$
5052 measured reflections
4773 independent reflections
3022 reflections with $I > 2\sigma(I)$

$R_{int} = 0.097$
$\theta_{max} = 26.51°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 23$
$l = -19 \rightarrow 15$
3 standard reflections
  frequency: 60 min
  intensity decay: 1%

Refinement

Refinement on F^2
$R(F) = 0.068$
$wR(F^2) = 0.185$
$S = 1.033$
4773 reflections
286 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0801P)^2 + 29.94P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.043$
$\Delta\rho_{max} = 1.45$ e Å^{-3}
$\Delta\rho_{min} = -1.83$ e Å^{-3}

Table 5
Selected geometric parameters (Å, °) for (IV).

Re1—O1	2.019 (11)	Re1—O4	1.919 (2)
Re1—O2	2.027 (11)	Re1—N1	2.145 (13)
Re1—O3	1.696 (12)	Re1—N2	2.136 (14)
O1—Re1—O2	81.5 (5)	O2—Re1—N2	90.1 (5)
O1—Re1—O3	99.8 (5)	O3—Re1—O4	168.4 (3)
O1—Re1—O4	89.7 (3)	O3—Re1—N1	89.6 (5)
O1—Re1—N1	90.6 (5)	O3—Re1—N2	87.6 (6)
O1—Re1—N2	169.6 (6)	O4—Re1—N1	83.5 (4)
O2—Re1—O3	98.7 (5)	O4—Re1—N2	83.9 (4)
O2—Re1—O4	89.3 (3)	N1—Re1—N2	96.8 (5)
O2—Re1—N1	169.5 (4)		

Table 6
Hydrogen-bonding and C—H$\cdots$O contact geometry (Å, °) for (IV).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C9—H9$A\cdots$O1^i	0.99	2.55	3.46 (3)	152
C18—H18$\cdots$O1	1.00	2.28	3.180 (18)	149
C18—H18$\cdots$O2	1.00	2.36	3.14 (2)	134
C19—H19$\cdots$O3	1.00	2.17	3.10 (2)	154

Symmetry code: (i) $-x, -y, -z$.

Huub Kooijman *et al.* • Polymorphs and pseudo-polymorphs of $[Re_2O(C_{17}H_{16}N_2O_3)_2]$

metal-organic compounds

Compound (V)

Crystal data

$[Re_2O(C_{17}H_{16}N_2O_3)_2]\cdot 2CHCl_3$	$Z = 1$
$M_r = 1219.79$	$D_x = 2.047$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.0223$ (12) Å	Cell parameters from 25
$b = 10.4856$ (15) Å	reflections
$c = 10.7375$ (17) Å	$\theta = 9.81–13.97°$
$\alpha = 79.750$ (12)°	$\mu = 6.57$ mm^{-1}
$\beta = 89.256$ (11)°	$T = 150$ K
$\gamma = 81.820$ (11)°	Block, dark green
$V = 989.4$ (3) Å^3	$0.40 \times 0.40 \times 0.15$ mm

Data collection

CAD-4T diffractometer	$R_{int} = 0.073$
ω scans	$\theta_{max} = 26.46°$
Absorption correction: ψ scan	$h = -11 \rightarrow 10$
(PLATON; Spek, 2000)	$k = -12 \rightarrow 0$
$T_{min} = 0.256$, $T_{max} = 0.373$	$l = -12 \rightarrow 12$
3862 measured reflections	3 standard reflections
3648 independent reflections	frequency: 60 min
3333 reflections with $I > 2\sigma(I)$	intensity decay: 3%

Refinement

Refinement on F^2	H atoms: see below
$R(F) = 0.028$	$w = 1/[\sigma^2(F_o^2) + (0.0487P)^2 + 0.28P]$
$wR(F^2) = 0.070$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.047$	$(\Delta/\sigma)_{max} = 0.001$
3648 reflections	$\Delta\rho_{max} = 2.74$ e Å^{-3}
250 parameters	$\Delta\rho_{min} = -1.65$ e Å^{-3}

Table 7
Selected geometric parameters (Å, °) for (V).

Re1—O1	2.000 (3)	Re1—O4	1.9106 (4)
Re1—O2	2.001 (3)	Re1—N1	2.097 (4)
Re1—O3	1.699 (4)	Re1—N2	2.128 (4)
O1—Re1—O2	80.93 (13)	O2—Re1—N2	91.56 (15)
O1—Re1—O3	99.16 (17)	O3—Re1—O4	168.32 (14)
O1—Re1—O4	90.24 (10)	O3—Re1—N1	89.67 (19)
O1—Re1—N1	91.31 (15)	O3—Re1—N2	89.13 (18)
O1—Re1—N2	169.48 (15)	O4—Re1—N1	83.16 (12)
O2—Re1—O3	98.03 (17)	O4—Re1—N2	82.39 (12)
O2—Re1—O4	90.25 (10)	N1—Re1—N2	95.23 (16)
O2—Re1—N1	169.82 (16)		

Table 8
Hydrogen-bonding and C—H⋯O contact geometry (Å, °) for (V).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C9—H9B⋯O2^i	0.99	2.56	3.465 (7)	153
C13—H13⋯O3^{ii}	0.95	2.58	3.212 (7)	124
C18—H18⋯O1	1.00	2.43	3.216 (7)	135
C18—H18⋯O2	1.00	2.25	3.167 (7)	151
C18—H18⋯O3	1.00	2.69	3.444 (7)	133

Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $1 - x, -y, 1 - z$.

Compound (VI)

Crystal data

$[Re_2O(C_{17}H_{16}N_2O_3)_2]\cdot 2CH_2Cl_2$	$Z = 1$
$M_r = 1150.91$	$D_x = 2.008$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.9642$ (16) Å	Cell parameters from 25
$b = 10.053$ (3) Å	reflections
$c = 10.669$ (3) Å	$\theta = 11.53–13.92°$
$\alpha = 91.23$ (2)°	$\mu = 6.69$ mm^{-1}
$\beta = 91.685$ (18)°	$T = 150$ K
$\gamma = 97.913$ (17)°	Plate, dark green
$V = 951.6$ (4) Å^3	$0.5 \times 0.3 \times 0.1$ mm

Data collection

Enraf–Nonius CAD-4T diffractometer	$R_{int} = 0.086$
	$\theta_{max} = 27.50°$
ω scans	$h = -7 \rightarrow 11$
Absorption correction: ψ scan	$k = -13 \rightarrow 12$
(PLATON; Spek, 2000)	$l = -13 \rightarrow 13$
$T_{min} = 0.154$, $T_{max} = 0.512$	3 standard reflections
4978 measured reflections	frequency: 60 min
4361 independent reflections	intensity decay: 2%
4148 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	H atoms: see below
$R(F) = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.1052P)^2 + 2.57P]$
$wR(F^2) = 0.137$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.060$	$(\Delta/\sigma)_{max} = 0.001$
4361 reflections	$\Delta\rho_{max} = 2.45$ e Å^{-3}
245 parameters	$\Delta\rho_{min} = -3.81$ e Å^{-3}

Table 9
Selected geometric parameters (Å, °) for (VI).

Re1—O1	2.014 (6)	Re1—O4	1.9090 (6)
Re1—O2	1.999 (5)	Re1—N1	2.109 (7)
Re1—O3	1.697 (5)	Re1—N2	2.133 (7)
O1—Re1—O2	81.5 (2)	O2—Re1—N2	91.1 (2)
O1—Re1—O3	99.5 (2)	O3—Re1—O4	166.81 (17)
O1—Re1—O4	91.24 (16)	O3—Re1—N1	88.8 (3)
O1—Re1—N1	91.0 (2)	O3—Re1—N2	87.9 (2)
O1—Re1—N2	170.2 (2)	O4—Re1—N1	83.3 (2)
O2—Re1—O3	98.5 (2)	O4—Re1—N2	82.34 (17)
O2—Re1—O4	90.60 (16)	N1—Re1—N2	95.6 (3)
O2—Re1—N1	170.3 (3)		

Table 10
Hydrogen-bonding and C—H⋯O contact geometry (Å, °) for (VI).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C4—H4⋯O3^i	0.95	2.53	3.296 (9)	138
C9—H9B⋯O1^{ii}	0.99	2.68	3.569 (12)	149
C9—H9B⋯O2^{ii}	0.99	2.64	3.542 (12)	151
C11—H11⋯O3^{iii}	0.95	2.54	3.128 (9)	120
C18—H18A⋯O3	0.99	2.55	3.195 (11)	123
C18—H18B⋯O2	0.99	2.35	3.258 (12)	152
C18—H18D⋯O1	0.99	2.38	3.269 (12)	150
C18—H18D⋯O3	0.99	2.45	3.195 (11)	132

Symmetry codes: (i) $-x, 1 - y, -z$; (ii) $-x, 1 - y, 1 - z$; (iii) $1 - x, 1 - y, 1 - z$.

Compound (VII)

Crystal data

$[Re_2O(C_{17}H_{16}N_2O_3)_2]\cdot 2H_2O$	$D_x = 2.124$ Mg m^{-3}
$M_r = 1017.09$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25
$a = 10.1085$ (8) Å	reflections
$b = 11.2053$ (8) Å	$\theta = 11.68–13.98°$
$c = 14.0447$ (7) Å	$\mu = 7.669$ mm^{-1}
$\beta = 91.367$ (5)°	$T = 150$ K
$V = 1590.37$ (19) Å^3	Block, dark green
$Z = 2$	$0.24 \times 0.09 \times 0.07$ mm

Data collection

Enraf–Nonius CAD-4T diffractometer	$R_{int} = 0.145$
	$\theta_{max} = 27.49°$
ω scans	$h = -13 \rightarrow 13$
Absorption correction: ψ scan	$k = -14 \rightarrow 0$
(PLATON; Spek, 2000)	$l = -18 \rightarrow 18$
$T_{min} = 0.149$, $T_{max} = 0.615$	3 standard reflections
7271 measured reflections	frequency: 60 min
3639 independent reflections	intensity decay: 5%
3143 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.008P)^2 + 4.5P]$
$R(F) = 0.047$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.101$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.010$	$\Delta\rho_{max} = 2.21$ e Å^{-3}
3639 reflections	$\Delta\rho_{min} = -2.94$ e Å^{-3}
227 parameters	Extinction correction: *SHELXL*97
H atoms: see below	(Sheldrick, 1997)
	Extinction coefficient: 0.0033 (2)

Table 11
Selected geometric parameters (Å, °) for (VII).

Re1—O1	2.020 (5)	Re1—O4	1.9129 (3)
Re1—O2	1.996 (5)	Re1—N1	2.135 (6)
Re1—O3	1.724 (7)	Re1—N2	2.130 (5)
O1—Re1—O2	80.25 (18)	O2—Re1—N1	168.5 (2)
O1—Re1—O3	98.2 (2)	O2—Re1—N2	92.0 (2)
O1—Re1—O4	91.23 (16)	O3—Re1—O4	165.92 (18)
O1—Re1—N1	91.7 (2)	O3—Re1—N1	88.8 (3)
O1—Re1—N2	170.1 (2)	O3—Re1—N2	89.2 (2)
O2—Re1—O3	100.3 (3)	O4—Re1—N1	80.43 (18)
O2—Re1—O4	91.54 (16)	O4—Re1—N2	82.78 (19)

Table 12
Hydrogen-bonding and C—H···O contact geometry (Å, °) for (VII).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H51···O3[i]	0.85	2.30	2.981 (8)	137
O5—H52···O1	0.85	2.37	3.158 (8)	154
O5—H52···O2	0.85	2.35	2.975 (7)	131
C3—H3···O5[ii]	0.95	2.55	3.268 (11)	133
C9—H9B···O5[iii]	0.99	2.52	3.429 (12)	152
C11—H11···O3[iii]	0.95	2.48	3.379 (9)	158

Symmetry codes: (i) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $-x, 1 - y, -z$; (iii) $-x, y - \frac{1}{2}, \frac{1}{2} - z$.

All ordered non-H atoms were refined with anisotropic displacement parameters. The minor disorder component positions of modifications (III) and (VI) were assigned an isotropic displacement parameter set equal to the equivalent isotropic displacement parameter of the major component. All H atoms bonded to C were included in the refinement at calculated positions, riding on their carrier atoms. Their isotropic displacement parameters were fixed at 1.2 times the value of the equivalent isotropic displacement parameter of their carrier atom. For modification (IV), broad highly structured reflection profiles of varying width were observed, which is indicative of a crystal consisting of several slightly misaligned individuals. Each reflection was measured at the ψ angle for which the minimal profile width can be expected; the A-vector method (Duisenberg, 1983) was used to calculate this ψ angle. The measured crystal consisted of at least four individuals, slightly rotated over vector ($-0.095, 0.930, 0.356$). An analytical absorption correction procedure could not be applied because the description of the crystal in terms of bounding lattice planes was not accurate enough due to the irregular crystal shape. A ψ-scan correction was not appropiate

because of the anisotropic split of the reflections. Since the transmission factors obtained from an empirical correction based on ΔF fall well within the range of values calculated from the absorption coefficient and the rough crystal dimensions, this method was applied. A difference Fourier map showed the water-H atoms of modification (VII) to be in hydrogen-bonding positions with O1, O2 and O3. Since free refinement of the H atoms proved to be unstable, the water molecule was refined as a rigid group, with the H atoms at idealized positions and oxygen as the pivot atom. Weak distance restraints were necessary to keep the H atoms in hydrogen-bonding positions. The isotropic displacement parameters of H atoms bonded to O were fixed at 1.5 times the value of the equivalent isotropic displacement parameter of the O atom. A mild restraint was applied to prevent unrealistic anisotropy of the salicylidene O-atom displacement parameters.

For compounds (II) and (III), data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; for compounds (IV), (V), (VI) and (VII), data collection: locally modified *CAD*-4 *Software* (Enraf–Nonius, 1983); cell refinement: *SET*4 (de Boer & Diusenberg. 1984); data reduction: *HELENA* (Spek, 1997); for all compounds, program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *PLATON*.

References

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.
Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* A**40**, C-410.
Bommel, K. J. C. van, Verboom, W., Kooijman, H., Spek, A. L. & Reinhoudt, D. N. (1998). *Inorg. Chem.* **37**, 4197–4203.
Buchler, J. W. & Kruppa, J. B. (1990). *Z. Naturforsch. Teil B*, **45**, 518–530.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Duisenberg, A. J. M. (1983). *Acta Cryst.* A**39**, 211–215.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Kitaigorodskii, A. I. (1961). *Organic Chemical Crystallography*, pp. 106–109. New York: Consultants Bureau.
Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
Pillai, M. R. A., Barnes, C. L. & Schlemper, E. O. (1994). *Polyhedron*, **13**, 701–708.
Reisgys, M., Spies, H., Johannsen, B., Leibnitz, P. & Pietzsch, H. J. (1997). *Chem. Ber.* **130**, 1343–1347.
Sheldrick, G. M. (1985). *SHELXS*86. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (1997). *HELENA*. University of Utrecht, The Netherlands.
Spek, A. L. (2000). *PLATON*. University of Utrecht, The Netherlands. Internet: http://www.cryst.chem.uu.nl/platon/