Molecular complexes of dimethyl sulfoxide with tri- and dichloromethane[1]

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Crystals of molecular complexes of dimethyl sulfoxide with trichloromethane (chloroform), $(CH_3)_2SO\cdot2CHCl_3$, (I), and dichloromethane, $(CH_3)_2SO\cdot CH_2Cl_2$, (II), have been grown *in situ*. In both compounds, the components are linked together by $(Cl)C—H\cdots O$ interactions. The dimethyl sulfoxide molecules in (I) are bound into chains by $C—H\cdots O$ interactions. In (II), pairs of the components form centrosymmetric rings, linked into a three-dimensional network by $C—H\cdots O$ contacts and dipole–dipole interactions between dimethyl sulfoxide molecules.

Comment

The cryocrystallization method for the structural study of compounds which are not solid under ambient conditions has attracted increasing attention in recent years. This technique, consisting of *in situ* crystallization of the system under investigation followed by a single-crystal X-ray study of the crystals obtained, is nowadays used not only for studying pure compounds, but also for the synthesis of new polymorphs (Choudhury *et al.*, 2004; Ibberson *et al.*, 2008) and cocrystals (Wiechert & Mootz, 1999; Bond, 2003), and for studies of isotope effects (Crawford *et al.*, 2009; Vasylyeva *et al.*, 2010). Liquid chemical systems are usually made up of relatively small molecules and thus represent good models for theoretical calculations. They also reveal a variety of intermolecular interactions and their structures are far from being intuitively predictable. Previously, we have shown that the common organic solvents chloroform (trichloromethane, CF) and dichloromethane (DCM) are able to form low-melting molecular complexes (LmMCs) with various small organic ketones, 1,4-dioxane, triethylamine and *N,N*-dimethylformamide (Yufit & Howard, 2010, 2012). We report here the synthesis and structures of two new LmMCs of dimethyl sulfoxide (DMSO) with CF, (I), and DCM, (II).

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[1] *Low-melting molecular complexes*, Part 3. For Part 2, see Yufit & Howard (2012).

LmMC structure (I) (crystallized from a 3:1 molar ratio mixture of CF and DMSO) contains two CF molecules per molecule of DMSO (Fig. 1). Interestingly enough, the existence of 2:1 CF–DMSO aggregates linked by $Cl_3C—H\cdots O$ interactions in solution was predicted by spectroscopic methods (Daniel & McHale, 1997), although their exact

(I)   (II)
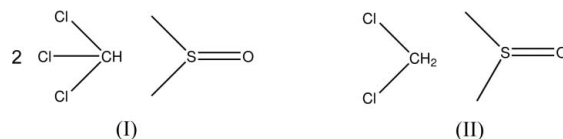
geometry remained unknown. According to the spectroscopic data, 1:1 aggregates are also present in solution, but all our attempts to crystallize them have failed so far: any increase in the relative concentration of DMSO in the mixture results in the crystallization of pure α-DMSO. The CF molecules of (I) are indeed connected to the DMSO molecule by weak $Cl_3C—H\cdots O$ hydrogen bonds. A similar motif has been observed before in the LmMC of CF with butan-2-one (methyl ethyl ketone, MEK) (Yufit & Howard, 2012), in which these interactions were different for CF molecules located in and out of the plane of the MEK molecule. In the case of (I), the geometry of both contacts is almost identical. The DMSO molecules in (I) are linked together in chains parallel to the [100] direction by $C—H\cdots O(x − 1, y, z)$ contacts (Fig. 2). A similar arrangement of DMSO molecules was found in the structure of α-DMSO (Thomas *et al.*, 1966), where a number of
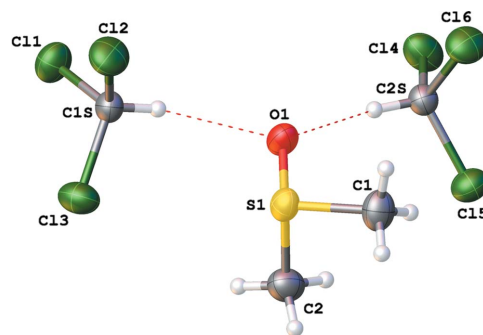
Figure 1
The molecular structure and atom-labelling scheme for (I). Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds.
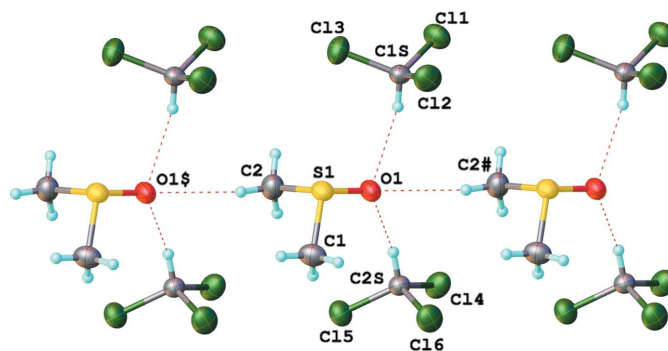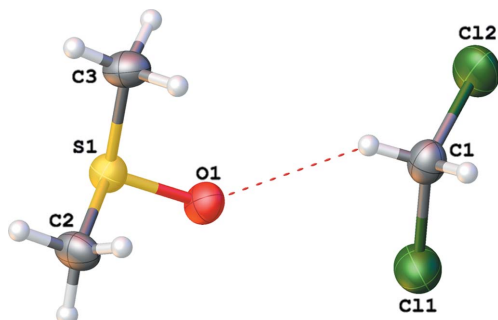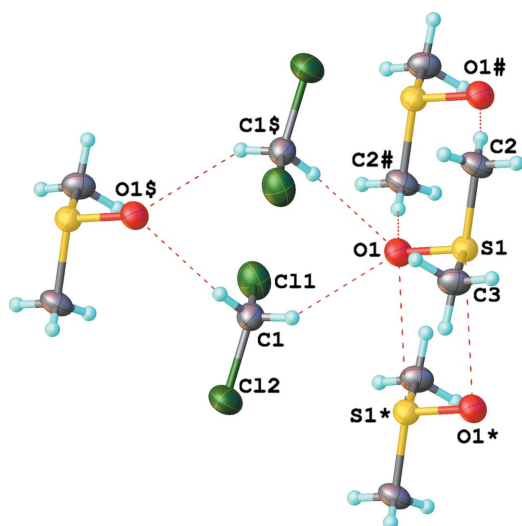
Figure 2
The chains in the structure of (I). Dashed lines indicate hydrogen bonds. [Symmetry codes: ($) $x − 1, y, z$; (#) $x + 1, y, z$.]

organic compounds

Figure 3
The molecular structure and atom-labelling scheme for (II). Displacement ellipsoids are drawn at the 50% probability level. The dashed line indicates a hydrogen bond.

other contacts of various types also exist. There are no direction-specific interactions between adjacent chains, the shortest inter-chain contact being Cl2···Cl2($-x + 2$, $-y + 1$, $-z + 1$) of 3.5290 (9) Å. This distance is slightly shorter than the shortest contact in the structure of pure CF [3.5669 (3) Å; Yufit & Howard, 2010].

In contrast with (I), LmMC structure (II) contains only one DCM molecule per DMSO molecule (Fig. 3), in spite of the fact that (II) was crystallized from a 4:1 molar ratio mixture of the components. Similar to the crystallization of (I), an increase in the relative concentration of DMSO in the mixture results in the crystallization of pure α-DMSO. The 1:1 composition of complex (II) reflects the difference between the H-atom-donor capacity of CF (one available H atom) and DCM (two H atoms). The components of (II) are also connected by Cl$_2$C—H···O interactions but they are slightly longer than those in (I), which is consistent with the lower H-acidity of DCM compared with that of CF. These contacts bind the components into centrosymmetric rings of $R_4^2(8)$ type (Etter *et al.*, 1990) (Fig. 4), similar to those found previously in the LmMC of DCM with cyclohexanone (Yufit & Howard, 2012). These cyclic dimers are linked into a three-dimensional

Figure 4
A fragment of the structure of (II), showing the intermolecular interactions as dashed lines. [Symmetry codes: ($) $-x + 1$, $-y + 1$, $-z + 1$; (#) $-x + 1$, $-y + 2$, $-z + 1$; (*) $-x$, $-y + 2$, $-z + 1$.]
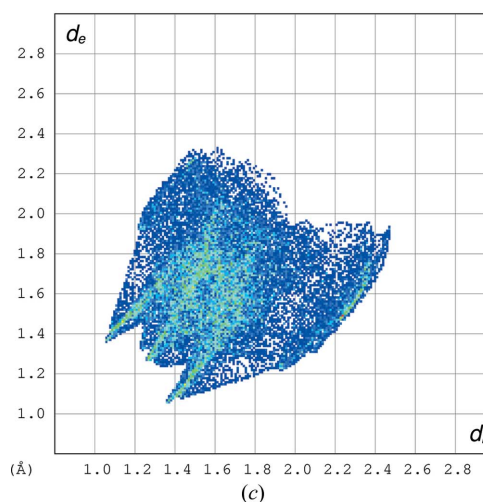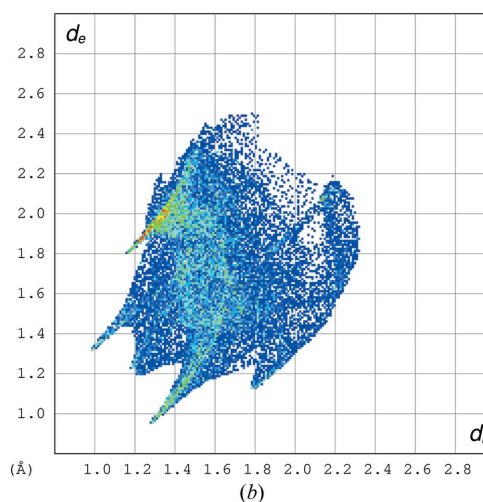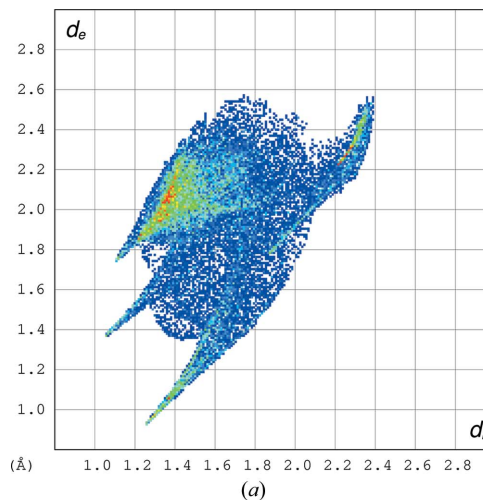
Figure 5
Fingerprint plots of the Hirshfeld surfaces of the DMSO molecules in (*a*) (I), (*b*) (II) and (*c*) α-DMSO. d_i and d_e are the distances from a point on the surface to the nearest nuclei inside and outside the surface, respectively.

network by interactions between the DMSO molecules. These interactions are of two types: a pair of C—H···O($-x + 1$, $-y + 1$, $-z + 1$) contacts connects DMSO molecules in the

[110] direction, while in the [100] direction the S=O groups of adjacent DMSO molecules are antiparallel and the corresponding S···O($-x$, $-y + 2$, $-z + 1$) distance is 3.2852 (19) Å. This implies the presence of a dipole–dipole interaction between these molecules. Remarkably, both types of contact are also present in the structure of α-DMSO (Thomas *et al.*, 1966). These interactions combine the centrosymmetric rings into layers parallel to the [110] direction. The shortest contact between the layers is Cl1···Cl1($-x + 1$, $-y + 1$, $-z + 2$) of 3.5149 (16) Å.

As noted earlier (Yufit & Howard, 2012), in some cases cocrystals retain particular features of the crystal structures of the pure components, and the composition of these particular fragments depends on the cocrystallization partner. In the case of LmMC structures (I) and (II), the CF 'selects' the chains of DMSO molecules from the structure of pure DMSO, while cocrystallization with DMC keeps the layers of DMSO molecules intact, breaking down the chains. The difference in the crystal environment of the DMSO molecules in (I), (II) and pure DMSO (Thomas *et al.*, 1966) becomes more apparent in Fig. 5, where a comparison of fingerprint plots of Hirshfeld surfaces (Spackman & McKinnon, 2002) is presented. The plots represent points on the Hirshfeld surface as a function of the closest distance from each such point to nuclei inside (d_i) and outside (d_e) the surface, thus showing all intermolecular interactions simultaneously. The plots for (I) and (II) are distinctively asymmetrical, which is typical for cocrystals. It is easy to see that the shortest intermolecular contacts in (I) and (II), the characteristic spurs on the plots, corresponding to (Cl)C—H···O interactions, are shorter than the shortest C—H···O contacts in pure DMSO (Thomas *et al.*, 1966).

Experimental

Mixtures of CF and DCM with DMSO (in 3:1 and 4:1 molar ratios, respectively) were sealed in 0.3 mm borosilicate glass capillaries which were mounted on a diffractometer using a special attachment (Yufit & Howard, 2005). The first mixture was cooled to 130 K and then warmed to 161 K when spontaneous crystallization occurred. The polycrystalline sample of (I) obtained was warmed slowly to 198 K until only a few crystalline seeds could be seen in the capillary, and was then cooled slowly to 185 K. The data were collected at this temperature. The second mixture solidified at 130 K and a suitable crystal of (II) grew at 167 K. The data were collected at this temperature. In both cases, several spatially separated crystals were present in the capillaries and the reflections from one of them were manually picked up for indexing and subsequent integration using the program *RLATT* (Bruker, 2000).

Compound (I)

Crystal data

2CHCl3·C2H6OS
$M_r = 316.86$
Monoclinic, $P2_1/n$
$a = 5.9679$ (3) Å
$b = 9.0041$ (6) Å
$c = 23.1424$ (15) Å
$\beta = 91.63$ (1)°

$V = 1243.07$ (13) Å³
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.51$ mm⁻¹
$T = 185$ K
0.4×0.15 (radius) mm

Table 1
Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1S—H1S···O1	0.922 (15)	2.365 (16)	3.1779 (18)	146.9 (13)
C2—H2C···O1ⁱ	0.95 (2)	2.53 (2)	3.389 (2)	149.9 (17)
C2S—H2S···O1	0.945 (16)	2.301 (16)	3.1897 (17)	156.4 (13)

Symmetry code: (i) $x - 1$, y, z.

Data collection

Bruker SMART 6000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2006)
$T_{min} = 0.437$, $T_{max} = 0.745$

10789 measured reflections
2883 independent reflections
2481 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.056$
$S = 1.04$
2883 reflections

141 parameters
All H-atom parameters refined
$\Delta\rho_{max} = 0.26$ e Å⁻³
$\Delta\rho_{min} = -0.25$ e Å⁻³

Compound (II)

Crystal data

CH2Cl2·C2H6OS
$M_r = 163.05$
Triclinic, $P\overline{1}$
$a = 6.6800$ (12) Å
$b = 7.7862$ (13) Å
$c = 8.0017$ (15) Å
$\alpha = 78.019$ (10)°
$\beta = 80.008$ (10)°

$\gamma = 65.665$ (10)°
$V = 369.13$ (11) Å³
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 1.06$ mm⁻¹
$T = 167$ K
0.4×0.15 (radius) mm

Data collection

Bruker SMART 6000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2006)
$T_{min} = 0.590$, $T_{max} = 0.970$

3271 measured reflections
1658 independent reflections
1306 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.113$
$S = 1.01$
1658 reflections

66 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.33$ e Å⁻³
$\Delta\rho_{min} = -0.44$ e Å⁻³

In both cases, the data were collected using two 180° ω scans in 0.3° steps. Between scans, the crystal was manually rotated by 180° around the ω axis. This data-collection mode is necessary because of the design of the mounting attachment and does not provide full coverage (Yufit & Howard, 2005); the data coverage was 0.795 ($\theta <$ 30°) of a full sphere for (I) and 0.770 ($\theta < 29.99°$) of a full sphere for

Table 2
Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1A···O1ⁱ	0.99	2.45	3.291 (3)	143
C1—H1B···O1ⁱ	0.99	2.33	3.243 (3)	153
C2—H2A···O1ⁱⁱ	0.98	2.40	3.363 (3)	166
C3—H3C···O1ⁱⁱⁱ	0.98	2.70	3.373 (3)	126

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

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(II). Two and eight reflections for structures (I) and (II), respectively, were omitted from the refinement as they overlapped with reflections from other crystals present in the capillaries.

The H atoms of (I) were located in a difference Fourier map and freely refined isotropically. The H atoms of (II) were placed in calculated positions and refined using a riding model, with C—H distances of 0.99 or 0.98 Å, and with U_{iso}(H) values of 1.2 or $1.5U_{eq}$(C), for methylene and methyl groups, respectively.

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) for (I); *smtbx-flip* (Bourhis *et al.*, 2009) for (II). For both compounds, program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3074). Services for accessing these data are described at the back of the journal.

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