

SUPPORTING INFORMATION

Two-step construction of molecular and polymeric mixed-metal Cu(Co)/Be complexes employing functionality of a pyridyl substituted acetylacetonate

Volodimir D. Vreshch,^a Alexander N. Chernega,^b Judith A.K. Howard,^c Joachim Sieler,^d and Konstantin V. Domasevitch*^{a #}

^a *Inorganic Chemistry Department, Kiev University, Volodimirska Street 64, Kiev 252033, Ukraine, # E-mail dk@anorgchemie.univ.kiev.ua*

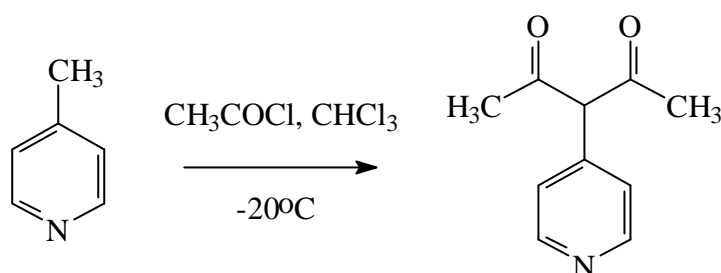
^b *Institute of Organic Chemistry, Murmanskaya St.4, Kiev 253660, Ukraine*

^c *Dept. of Chemistry, University of Durham, Durham, DH1 3LE, UK*

^d *Institut für Anorganische Chemie, Universität Leipzig, Linnéstraße 3, D-04103 Leipzig, Deutschland*

1. Synthesis

3-(4-pyridyl)-2,4-pentanedione (pyridylacetylacetonone):



L.G. Mackay, H.L. Anderson and J.K.M. Sanders, *J. Chem. Soc., Perkin Trans. 1*, 1995, 2269.

2. Crystallography

The intensity data for **2** were collected at 200K on a Stoe Image Plate Diffraction System [1] using MoK α graphite monochromated radiation ($\lambda = 0.71073 \text{ \AA}$): Image plate distance 70mm, ϕ oscillation scans $0 - 188.5^\circ$, step $\Delta\phi = 1.1^\circ$, θ range $2.52 - 25.88^\circ$, $d_{\max} - d_{\min} = 12.45 - 0.81 \text{ \AA}$. Measurements for structures **1**, **3-6** were made at 153K (1, 4, 6) and 223K (3, 5) using a Siemens SMART CCD area-detector diffractometer (graphite monochromated Mo-K α radiation, $\lambda = 0.71073 \text{ \AA}$, omega scans, $\Delta\omega 0.2^\circ$, exposition time 30 sec per frame, empirical absorption corrections using SADABS). The data frames were integrated using SAINT. The structures were solved by direct methods and refined by least-squares techniques using SHELXS-86 [2] and SHELXL-93 [3]. Details are given below.

Graphical representation of the crystal structures was made using program Diamond [4].

1. Stoe & Cie (2000). *IPDS Software*. Stoe & Cie GmbH, Darmstadt, Germany.
2. G.M. Sheldrick, *Acta Crystallogr.*, 1990, **A46**, 467.
3. G.M. Sheldrick, SHELXL93, A system of computer programs for X-ray structure determination, University of Göttingen, Göttingen, Germany, 1993.
4. K. Brandenburg, Diamond 2.1c, Crystal Impact GbR, Bonn, 1999.

Refinement of structures 2, 4, 5.

The refinements were standard. All non-hydrogen atoms were refined anisotropically, all CH hydrogens were placed in calculated positions with isotropic U values 1.2 times greater than U(eq) value of corresponding non-hydrogen atom. In structure **2** the solvate water molecule occupies a special position and only one unique OH hydrogen atom was located and refined isotropically.

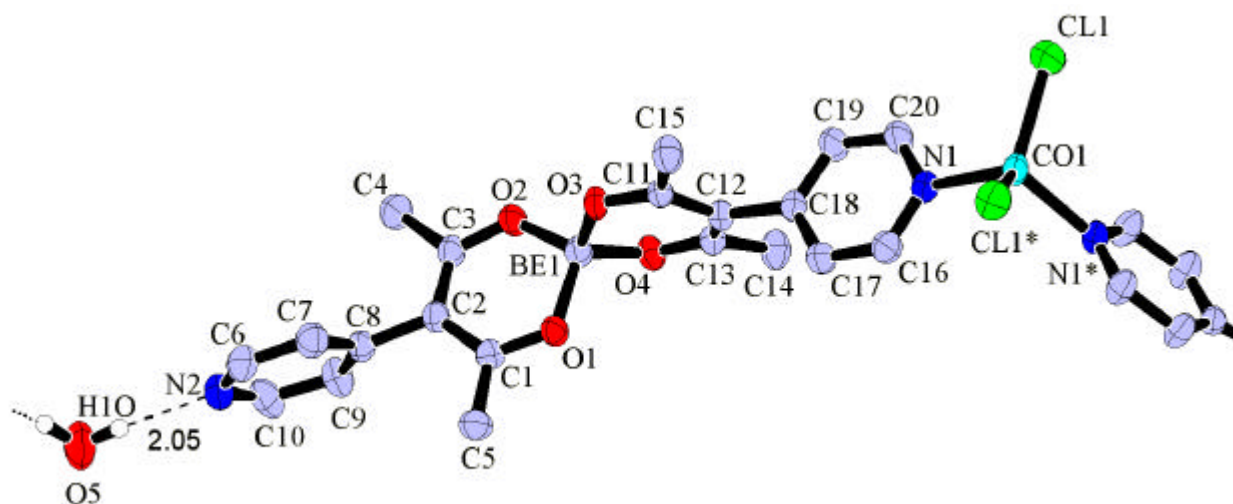


Fig. 1. Atom labelling scheme for structure **2**. 50% Thermal ellipsoids. Cobalt atom and oxygen atom of solvate water are situated in special positions (site letter 4e).

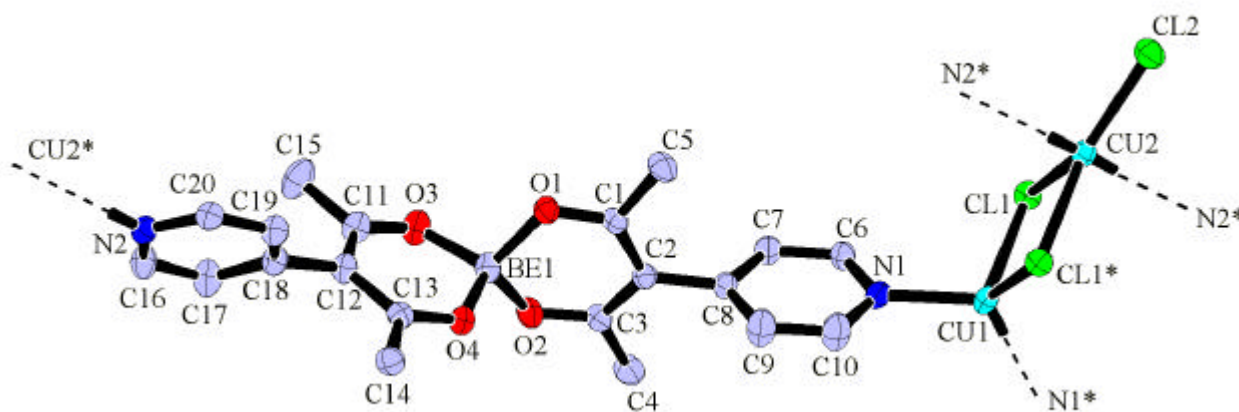


Fig. 2. Atom labelling scheme for structure **4** (and for structure **5** – bromine atoms instead of Cl). 50% Thermal ellipsoids. Atoms Cu1, Cu2 and Cl2 are situated in special positions (site letter 4e).

Refinement and proceeding of disorder in structure 1

All non-hydrogen atoms were refined anisotropically. Oxygen atom of solvate methanol molecule is unequally disordered over two positions (Fig. 3). Both contributions were refined anisotropically and no geometry constraints were used. OH hydrogen atom was located, but then fixed with $U(\text{iso}) 0.08 \text{ \AA}^2$. Geometry for disordered methanol was reasonable: C21-O5 1.40, C21-O5A 1.37 Å (only slightly shortened with respect of the normal value 1.43 Å); H1O-O5 0.88, H1O-O5A 0.99 Å. All other hydrogen atoms were idealized (Methyl hydrogen atoms of disordered methanol were idealized considering the major orientation of the oxygen atom) and included with fixed $U(\text{iso}) 0.08 \text{ \AA}^2$.

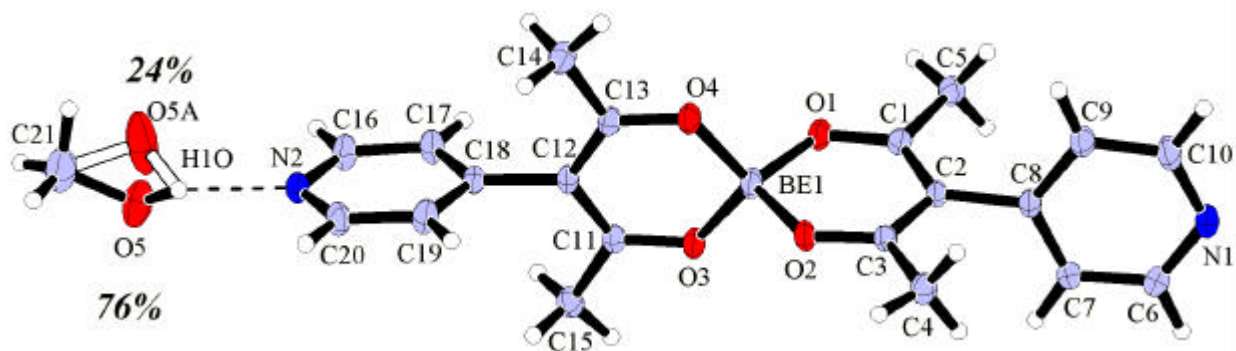


Fig. 3. Atom numbering scheme in structure 1, showing also refined disordering scheme for solvate methanol molecule. Thermal ellipsoids are at 50%.

Refinement and proceeding of disorder in structure 3

Unique part of the structure includes BeL_2 moiety, sulphate anion, two coordinated methanol molecules, non-coordinated water molecule and non-coordinated methanol molecule in general positions and two cobalt atoms situated in the centre of inversion.

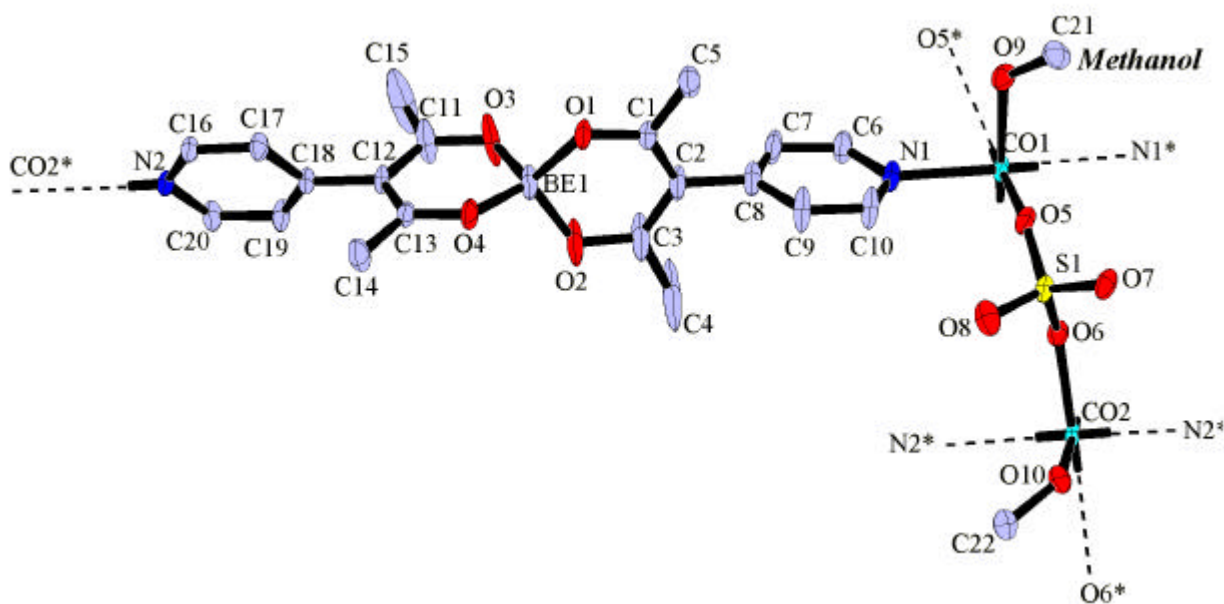


Fig. 4. Atom numbering scheme for structure 3. Thermal ellipsoids are drawn at 30% probability level. Note high anisotropy of thermal motion for C4 and C15 atoms.

Solvate methanol molecule is disordered over three overlapping positions. The disorder was resolved by constraining C-O bond length at $1.43(1) \text{ \AA}$ and equal partial occupancies for three sites (at 0.333). These atoms were refined anisotropically for the sake of overall convergence, and the resulting thermal parameters were almost normal (U_{eq} 0.073 to 0.122 \AA^2), with exception of atom C23A (U_{eq} 0.31 \AA^2 , U_{11} 0.45 \AA^2). It is important, however, that under present scheme all intermolecular contacts were

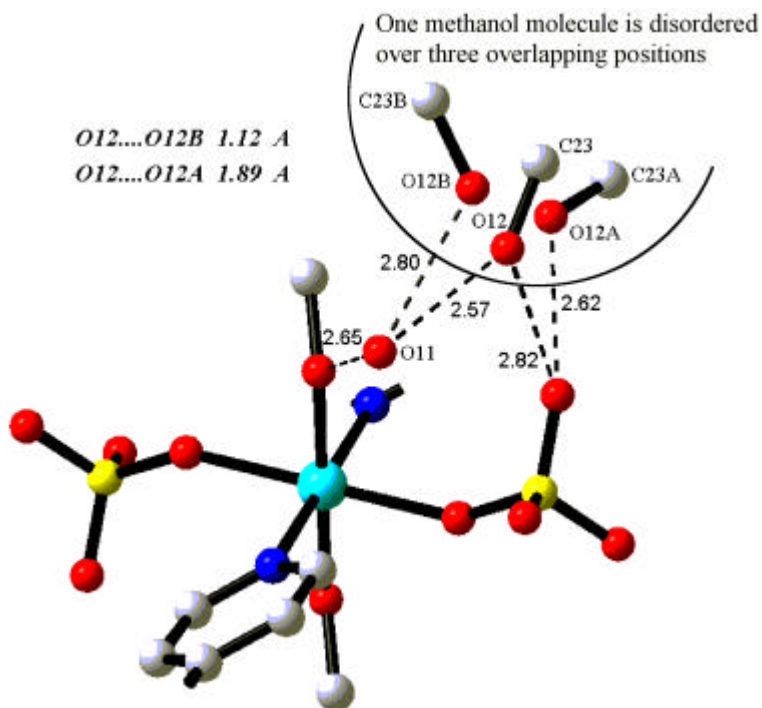


Fig. 5. Refined scheme for disorder of solvate methanol molecule in structure **3**. Note that the scheme affords very reasonable intermolecular contacts oxygen atoms of disordered methanol, coordinated methanol, solvate ester molecule (O11) and oxygen atom of sulphate group: O...O are within 2.57-2.82 Å that is typical for hydrogen bonding O-H...O.

highly reasonable and typical for hydrogen bonding, see Fig. 3. High anisotropy of thermal motion was registered also for side methyl carbon atoms of beryllium metalloligand C4 and C15 that may suggest possible rotational disorder of the “Be(acac)₂” spacer between two pyridyl rings. We were not successful to resolve it. For each of the ligands around beryllium atom the second acetyl group has normal thermal parameters. Thus all non-hydrogen atoms in the structure were refined anisotropically; the CH hydrogen atoms for BeL₂ and coordinated methanol were idealized and included with fixed U(iso) 0.08 Å²; OH hydrogens of coordinated methanol were located and then fixed with U(iso) 0.05 Å². Hydrogen atoms of solvate water molecule and of disordered solvate methanol were not included.

Refinement and proceeding of disorder in structure 6

Unique part for coordination portion of the structure is shown in Fig. 6. It comprises two unique “molecular rhombes” Cu₂Br₂ (centroid for one of them is situated in centre of inversion and only one Cu and one Br atoms are independent) and three unique BeL₂ moieties. Unique part includes also eight solvate chloroform molecules that gives composition of the clathrate **Cu₂Br₂{BeL₂}₂•5.33CHCl₃**. All non-hydrogen atoms for coordination portion were refined anisotropically; the hydrogen atoms were idealized and included with fixed U(iso) 0.08 Å².

Examination of residual electron density as well as thermal parameters for atoms of solvate chloroform molecules suggested disordering of the guests. Only three of eight unique chloroforms

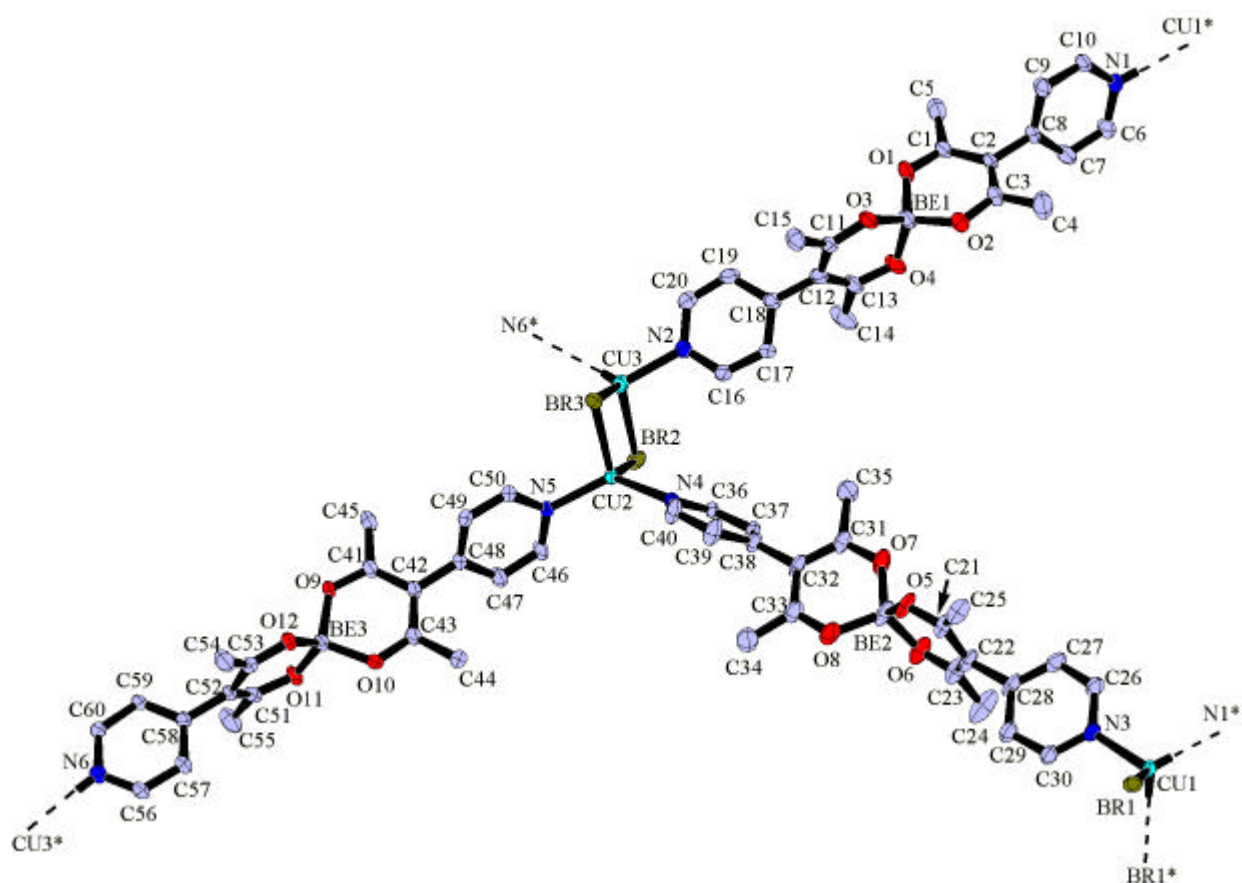


Fig. 6. Atom labelling scheme for structure **6**. 50% Thermal ellipsoids. Only unique part is shown (without chloroform of crystallization).

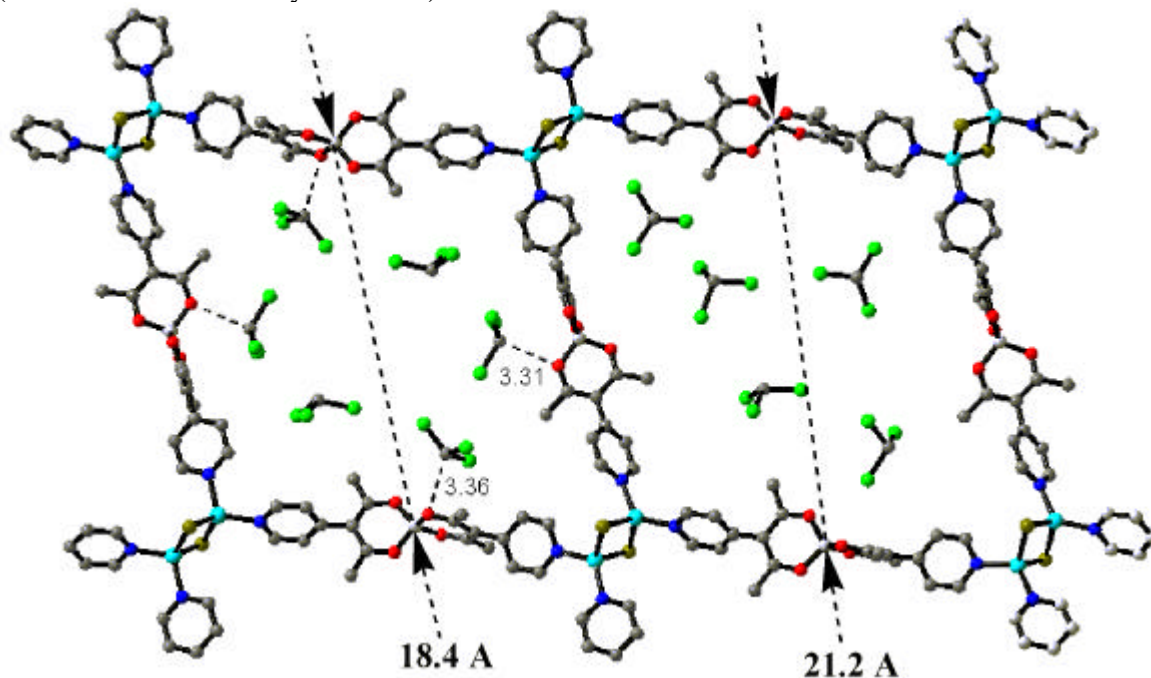


Fig. 7. Two different meshes in the structure of coordination polymer **6**: Centrosymmetric (left) and acentric (right). They incorporate different set of the guest chloroform molecules and it is interesting that the larger cage is populated by five guests, while the smaller one with six CHCl_3 molecules. In fact, six guests are packed much more dense (all Cl-Cl-Cl planes are orthogonal to the figure plane), and four of them also form weak H-bonds $\text{CH}\cdots\text{O}$ with carbonyl groups. Such H-bonding dictates orientation of the guests and the present chloroform molecules are ordered and the atoms possess normal thermal values.

possess relatively low parameters for thermal motion ($0.068\text{--}0.151 \text{ \AA}^2$). Atoms of these molecules (carbon atoms labels C1S, C2S, C4S) were refined anisotropically with no any restraints for geometry. Resulting C-Cl separations and Cl-C-Cl angles are normal, c.f. almost all C-Cl bonds are within $1.72\text{--}1.75 \text{ \AA}$ (min. $1.66(2)$, max. $1.82(1) \text{ \AA}$). In case of the other unique chloroform molecules the thermal motion is high and is very characteristic for guest molecules that are enclathrated inside large cages. A set of geometry constraints were applied in order to resolve the disorder and to improve the refinement stability. C-Cl bonds were set at $1.74(2) \text{ \AA}$ and intramolecular Cl...Cl contacts were set at $2.87(2) \text{ \AA}$ that correspond to a normal geometry of chloroform molecule. With such an approach, one more chloroform molecule was refined anisotropically (carbon atom C3S), resulting $U(\text{eq})$ values for the atoms are $0.085\text{--}0.36 \text{ \AA}^2$ and it was not possible to model the disorder in this case.

One of the molecules is disordered over two closely situated and overlapping positions – see Fig. 8, carbon atoms C7S, C9S, the partial contributions were 0.58 and 0.42. Atoms of a major component were refined anisotropically, while atoms of the minor component (C9S) were left isotropic and assigned with uniform isotropic thermal values that were refined as a single free variable. This afforded stable model for the refinement and allowed us to resolve the disorder in the present case. Another CHCl_3

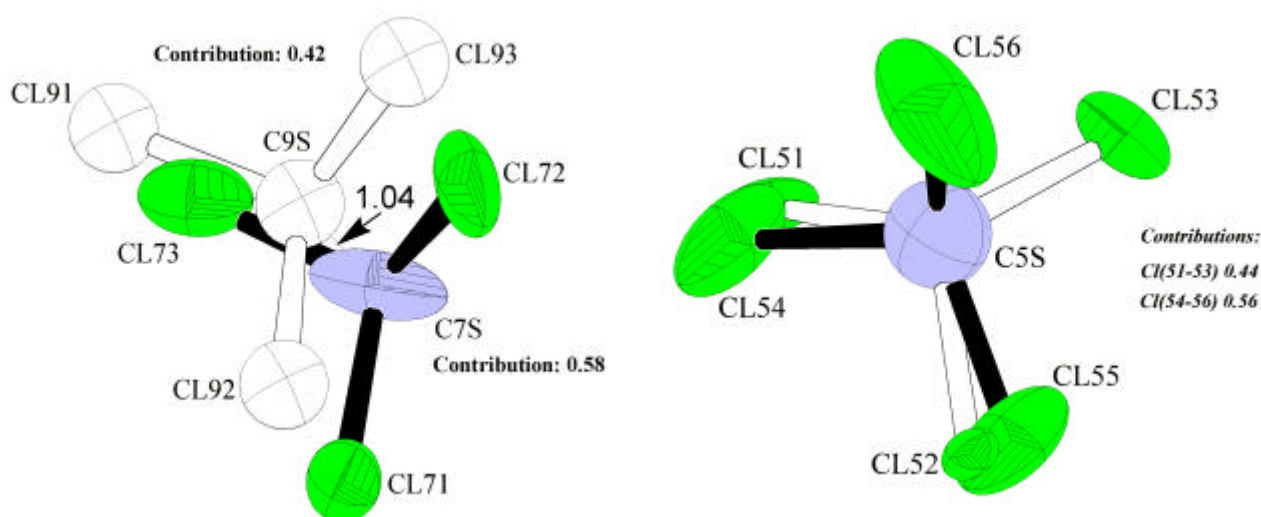


Fig. 8. Refined disordering scheme for two of 8 unique solvate chloroform molecules in structure 6. Thermal ellipsoids are at 30% probability level, isotropic atoms are shown as crossed circles. First molecule (left) is disordered over two closely situated (1.04 \AA) positions and the second one (right) shows orientation disorder of “ CCl_4 -type”.

molecule shows disordering of three chlorine atoms actually over four tetrahedral positions (around carbon atom C5S). Two components were resolved as shown in Fig. 8 (right) and only chlorine atoms were anisotropic. Finally, two remaining chloroform molecules were left isotropic (C6S, C8S, $U(\text{iso})$ values $0.16\text{--}0.34 \text{ \AA}^2$). Anisotropic refinement that was attempted in this case gave appr. 0.007 better R1 value, but led to unrealistic large thermal parameters for Cl atoms. Residual electron density map contains also several significant peaks ($1.0\text{--}1.8 \text{ e \AA}^3$) in the region of these chloroform molecules (C6S, C8S). This suggests that disorder in the structure was resolved only in part, but it was not possible to improve the model. No hydrogen atoms for the guest chloroform molecules were added in calculations.