Chapter 9.7

SYMMOL

TULLIO PILATI AND ALESSANDRA FORNI
C.N.R. - C.S.R.S.R.C.
VIA GOLGI, 19
I-20133 MILANO,ITALY
E-MAIL: PILA@SG1.CSRSRC.MI.CNR.IT
E-MAIL: AFORNI@RS18.CSRSRC.MI.CNR.IT

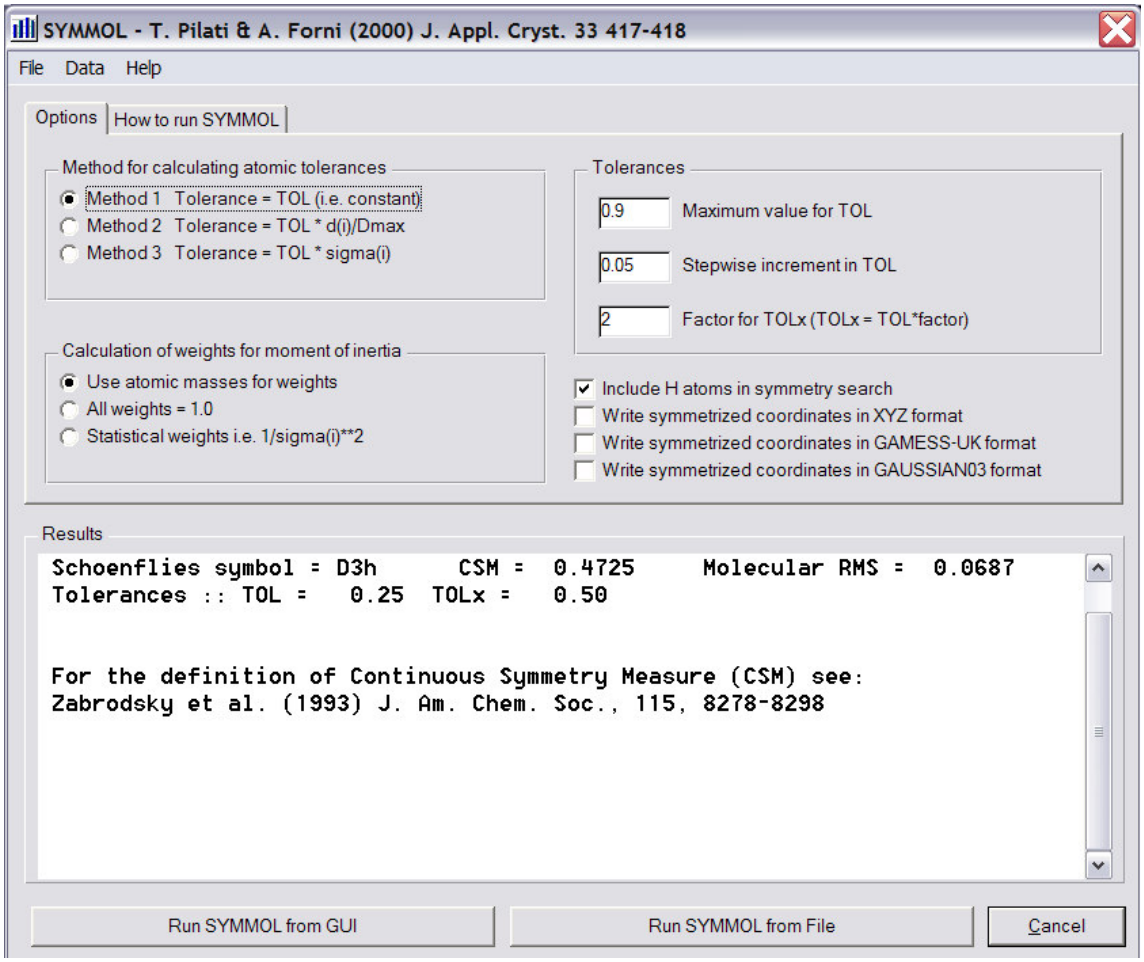
The program SYMMOL symmetrizes a group of atoms whose coordinates and errors are obtained from the *SHELXL.LST* file (or from a CIF). It prints out information about the given set of atoms and information concerning its symmetry: the symmetrized orthogonal coordinates together with the point group, the labels and the equivalent positions. Some quantities showing the goodness-of-fit are also printed: the rms on the coordinates, the molecular rms, the maximum deviation of the coordinates of the atom from the symmetrized ones and the continuous symmetry measure (CSM) for the whole point group and for the single elements of the point group. The CSM concept has been developed by Zabrodsky and Avnir and their coworkers (see *J. Am. Chem. Soc.*, (1993), **115**, 8278-8298). It provides a very useful *quantitative* measure of the true symmetry of a molecule as derived from the crystallographic coordinates.

For hexagonal point groups or for point groups other than the 32 crystallographic point groups, the program also prints out the symmetry group matrices in the orthogonal frame, the symmetry operations in hexagonal coordinates and the atom coordinates in the hexagonal system.

The symmetrization is performed within a tolerance TOL (called "DCM" in SYMMOL output file) based on a value given in input. The user may choose between different possible criteria of tolerance: the tolerance may be a constant, that is, the TOL input value, or a variable. In the latter case, the tolerance for each atom is TOL weighted by either the distance of the atom from the centre of mass or the mean standard uncertainty (s.u.) of the atom. Computation of the inertia moments may be performed using atomic masses as weights or assigning unitary weights to the atoms or weighting the atoms by the reciprocal of their mean square s.u.

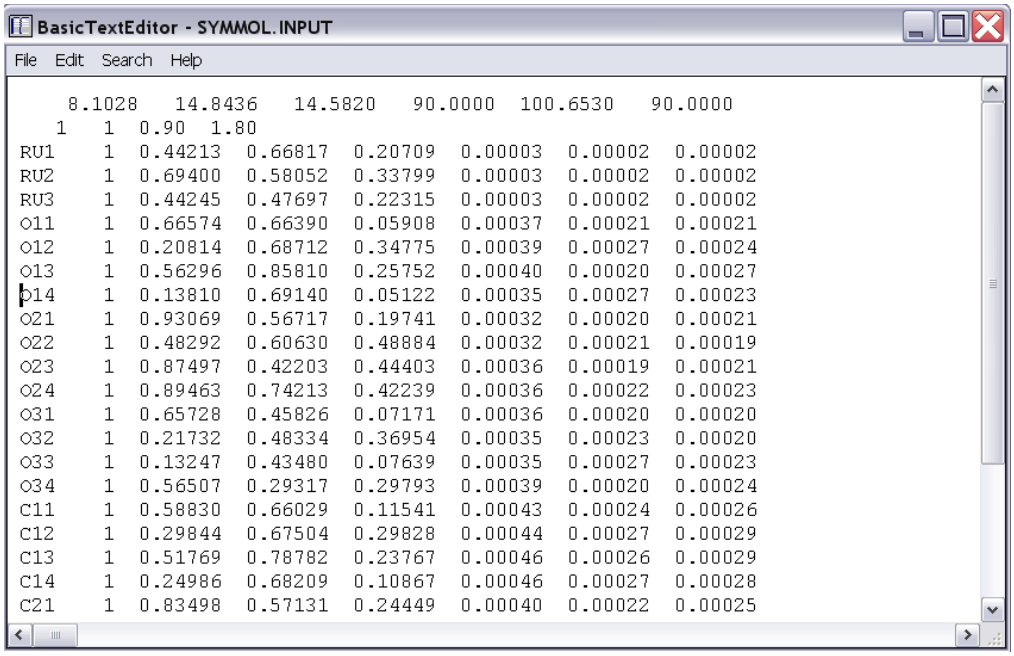
Atoms with IMOL less than 0 are not used to find the symmetry group, but, after symmetrization of atoms with IMOL = 1, the atoms with IMOL = -1 are examined to see if it is possible to symmetrize them in the same group, but according to the larger tolerance parameter TOLx (called "DCME" in SYMMOL output file). The use of IMOL less than 0 can be very useful when there is a pseudo degeneracy of the principal inertia axes

The GUI shown over the page opens when selecting this program. The first (automatic) run-through will search for higher and higher symmetry, starting with default settings of the tolerance parameters TOL & TOLx, up to a maximum of TOL (default 0.9). The start value of TOL is fixed at 0.05. It is possible to make adjustments to the default values of the parameters INDWGH, INDTOL, TOL, TOLx (meanings explained below). It is *very important* that the appropriate tolerances are set. The default values will generally result in found symmetry when TOL is high, but it will be necessary to modify these to stop the calculations at intermediate symmetries.



It may also be necessary to modify the IMOL(i) parameters for various atoms by editing the input file, using the Edit box shown below. The IMOL(i) parameter for each atom is the number immediately following the atom name. Setting a value of IMOL(i) for a particular atom to -1 removes this atom from the initial search.

USEFUL NOTE : Placing a hash (#) as the first symbol in a line comments out that line, and that atom is effectively deleted from all calculations.



9.7.1 Input information

The version of SYMMOL in WinGX writes the input file automatically, and it is only possible to edit the atom cards directly (using the above Edit Box) after the first default run. The other parameters are set using the GUI, and their detailed meaning is given below.

The input file format for SYMMOL is as follows;

```
(1) CELL PARAMETERS (free format)
   if orthogonal coordinates are given,  cell must be: 1 1 1 90 90 90

(2) INDWGH,INDTOL,TOL,TOLx (free format)

INDWGH=0,1 moments of inertia are calculated with weights = atomic masses

INDWGH=2   moments of inertia are calculated with weights = 1.0

INDWGH=3   moments of inertia are calculated with weights = (1/s(i))**2
              were s(i) = is the mean s.u. for the atom i as calculated
              from atomic standard uncertainties (see below)

INDTOL=0,1 an element of symmetry of the molecular group is accepted only
              if for any atom i exist an atom j for which
              ABS[XO(i)-Mk*XO(j)] less than TOL
              where XO are the inertial coordinates, Mk is the symmetry
              matrix and TOL is a constant tolerance

INDTOL=2   as indtol=1 but the tolerance is now TOL*d(i)/dm
              where d(i) is the distance of the atom i from the mass centre
              and dm is the mean of the d(i) of all the considered atom

INDTOL=3   as indtol=1 but the tolerance is now TOL*s(i)
```

```
(3) Atom cards
NAME(i) MOL(i) X(i) SX(i) for I=1 to NA=total number of atoms.
          format(a6,i2,6f9.5)

NAME(i) = Label for the atom i. The first (1 or 2) non-blank letters must
             be the symbol of the atomic species.
           - the symbol may be in upper lower case or mixed

MOL(i)  =   group (molecule) of atom i

The program attempts to symmetrize all the groups. With MOL(i) less than 0,
this atom belongs to the group ABS(MOL(i)) but it weight is 0.0 and the
tolerance for this atoms is TOLx

MOL(i)  = 0 This atom is completely ignored

X(i)    = atom coordinates referred to the cell

SX(i)   = atom standard uncertainties referred to the cell
```

9.7.2 The output files

A summary output appears in the main SYMMOL GUI Window shown above, indicating whether any symmetry has been found within the given tolerances. A text file SYMMOL.LST is also written which provides more details. Files containing the symmetrised orthogonal coordinates in XYZ format (SYMMOL.XYZ), GAMESS-UK format (GAMESS-UK.ORTH) and GAUSSIAN03 format (GAUSSIAN.ORTH) to 10 decimal places (*i.e.* suitable for accurate quantum calculations) may be optionally written as well. Only the files for the *last* calculation are written, so if you wish to stop at an earlier symmetry, reduce the maximum allowed value of TOL.

A sample output is shown below, for $Ru_3(CO)_{12}$ which has *idealised* D_{3h} symmetry. Using TOL=0.22 the point group C_3 is found (with CSM =0.411 and Mol RMS = 0.064). Raising TOL to 0.25 gives the point group C_{3h} (with CSM = 0.583 and Mol RMS = 0.0764). Finally using TOL = 0.040 gives the point group D_{3h} (with CSM = 0.644 and Mol RMS = 0.080). This example illustrates the use of gently increasing values of the tolerance factor TOL to ascertain the true symmetry. In this case, the next highest symmetry above $C1$ (according to the atomic coordinates) is C_3, though the generally accepted D_{3h} molecular symmetry has figures of merit which are only marginally higher.

The following (full) output file SYMMOL.LST results from the last example. The ORTEP view of $Ru_3(CO)_{12}$ indicating the labelling scheme is also shown. Note that for D_{3h} symmetry, the program has chosen Ru(1) and the carbonyls CO(11) and CO(12) as comprising the asymmetric unit.

```
                                    SYMMOL
 A Program for the Symmetrisation of Groups of Atoms
        By Tullio Pilati and Alessandra Forni
            Version June 2nd 1998
  ==================================================


  INDWGH=1 ===> weights as atomic mass
  INDTOL=1 ===> constant tolerance
  CONSTANTS OF TOLERANCE=  0.400  0.400


  Cell :
         a         b         c     alpha      beta     gamma     volume
   8.10280  14.84360  14.58200    90.000   100.653    90.000 1723.61814


  ATOM GROUP  INPUT COORDINATES AND THEIR S.U.

 RU1     1   0.80601  0.08051  0.66201  0.00003  0.00001  0.00001
 RU2     1   1.05754 -0.02304  0.77685  0.00003  0.00001  0.00001
 RU3     1   1.05785  0.16818  0.79292  0.00003  0.00001  0.00002
 O11     1   1.01745  0.10614  0.51109  0.00028  0.00017  0.00015
 O12     1   0.60546  0.24239  0.57749  0.00032  0.00018  0.00019
 O13     1   0.62488 -0.07798  0.55576  0.00032  0.00016  0.00017
 O14     1   0.56936  0.06726  0.80265  0.00028  0.00016  0.00017
 O21     1   1.28282 -0.01625  0.63061  0.00030  0.00019  0.00016
 O22     1   1.36789 -0.06543  0.92307  0.00032  0.00023  0.00019
 O23     1   0.93448 -0.20709  0.70197  0.00035  0.00017  0.00019
 O24     1   0.84244 -0.04144  0.92798  0.00031  0.00017  0.00016
 O31     1   1.29286  0.18695  0.65258  0.00034  0.00022  0.00020
 O32     1   0.93701  0.35842  0.74233  0.00035  0.00017  0.00021
 O33     1   1.36166  0.19141  0.94878  0.00032  0.00022  0.00018
 O34     1   0.83416  0.16365  0.94081  0.00032  0.00018  0.00017
 C11     1   0.94932  0.09538  0.57081  0.00035  0.00019  0.00020
 C12     1   0.67872  0.18216  0.60935  0.00035  0.00021  0.00020
 C13     1   0.69196 -0.01904  0.59469  0.00035  0.00021  0.00019
 C14     1   0.66575  0.07134  0.75562  0.00035  0.00018  0.00020
 C21     1   1.19553 -0.01347  0.68269  0.00037  0.00021  0.00020
 C22     1   1.25316 -0.04921  0.86981  0.00040  0.00024  0.00022
 C23     1   0.98068 -0.13847  0.73020  0.00039  0.00021  0.00022
 C24     1   0.91721 -0.02969  0.87051  0.00037  0.00019  0.00021
 C31     1   1.20150  0.17508  0.70177  0.00040  0.00022  0.00023
 C32     1   0.98189  0.28785  0.76200  0.00040  0.00022  0.00023
 C33     1   1.25010  0.18207  0.89144  0.00040  0.00023  0.00023
 C34     1   0.91222  0.16032  0.88458  0.00038  0.00020  0.00021

Principal moments of inertia and degree of degeneracy
         3773.9         3058.5         3046.3         1

    Orthogonalisation matrix
   -4.948535    7.975992   -6.688866
    2.764240   12.489454    5.086634
    5.790194    0.854138  -11.917212

Atom      orthogonal coordinates        Distance Tolerance

RU1        1.41408  -0.81317   0.00768   1.63123   0.40000
RU2       -1.42469  -0.82701   0.00707   1.64734   0.40000
RU3       -0.00854   1.64382  -0.01932   1.64396   0.40000
O11        1.58167  -0.67627   3.05239   3.50373   0.40000
O12        4.26300   0.22434  -0.00803   4.26891   0.40000
O13        1.75698  -3.83376   0.08973   4.21815   0.40000
O14        1.53875  -0.91743  -3.04993   3.53715   0.40000
O21       -1.50716  -0.86335   3.06005   3.51864   0.40000
```

```
O22       -4.27662   0.24521   0.02531   4.28372   0.40000
O23       -1.78284  -3.84675   0.02968   4.23992   0.40000
O24       -1.51791  -0.88266  -3.05517   3.52380   0.40000
O31       -0.08308   1.81401   3.02993   3.53242   0.40000
O32        2.44518   3.42845   0.04638   4.21133   0.40000
O33       -2.36920   3.56656  -0.09778   4.28288   0.40000
O34        0.07305   1.72117  -3.08083   3.52978   0.40000
C11        1.43353  -0.69521   1.93702   2.50806   0.40000
C12        3.20697  -0.16334  -0.01497   3.21116   0.40000
C13        1.63474  -2.71419   0.06454   3.16913   0.40000
C14        1.40888  -0.83925  -1.92786   2.53099   0.40000
C21       -1.40138  -0.80501   1.93635   2.52218   0.40000
C22       -3.22325  -0.14027   0.00957   3.22632   0.40000
C23       -1.65298  -2.71842   0.01938   3.18159   0.40000
C24       -1.40978  -0.82156  -1.92732   2.52527   0.40000
C31       -0.05468   1.66344   1.90459   2.52932   0.40000
C32        1.52865   2.77118   0.01155   3.16487   0.40000
C33       -1.50810   2.84986  -0.06837   3.22502   0.40000
C34        0.03632   1.60934  -1.96159   2.53754   0.40000

     Symmetrised orthogonal coordinates                Atomic r.m.s.
RU1    1  1.42101 -0.82042  0.00000    0.00663  0.00600  0.01268  *
RU2    1 -1.42101 -0.82042  0.00000    0.00663  0.00600  0.01268
RU3    1  0.00000  1.64084  0.00000    0.00565  0.00692  0.01268
O11    1  1.52012 -0.87764  3.05603    0.05792  0.08504  0.01508  *
O12    1  4.23880  0.31943  0.00000    0.03487  0.07476  0.05965  *
O13    1  1.84276 -3.83062  0.00000    0.08146  0.01302  0.05965
O14    1  1.52012 -0.87764 -3.05603    0.05792  0.08504  0.01508
O21    1 -1.52012 -0.87764  3.05603    0.05792  0.08504  0.01508
O22    1 -4.23880  0.31943  0.00000    0.03487  0.07476  0.05965
O23    1 -1.84276 -3.83062  0.00000    0.08146  0.01302  0.05965
O24    1 -1.52012 -0.87764 -3.05603    0.05792  0.08504  0.01508
O31    1  0.00000  1.75529  3.05603    0.09577  0.03762  0.01508
O32    1  2.39604  3.51119  0.00000    0.04854  0.06670  0.05965
O33    1 -2.39604  3.51119  0.00000    0.04854  0.06670  0.05965
O34    1  0.00000  1.75529 -3.05603    0.09577  0.03762  0.01508
C11    1  1.40762 -0.81269  1.93303    0.03421  0.04891  0.01689  *
C12    1  3.19470 -0.10254  0.00000    0.02435  0.04060  0.04014  *
C13    1  1.68616 -2.71542  0.00000    0.04607  0.01091  0.04014
C14    1  1.40762 -0.81269 -1.93303    0.03421  0.04891  0.01689
C21    1 -1.40762 -0.81269  1.93303    0.03421  0.04891  0.01689
C22    1 -3.19470 -0.10254  0.00000    0.02435  0.04060  0.04014
C23    1 -1.68616 -2.71542  0.00000    0.04607  0.01091  0.04014
C24    1 -1.40762 -0.81269 -1.93303    0.03421  0.04891  0.01689
C31    1  0.00000  1.62538  1.93303    0.05480  0.02365  0.01689
C32    1  1.50855  2.81796  0.00000    0.02543  0.03993  0.04014
C33    1 -1.50855  2.81796  0.00000    0.02543  0.03993  0.04014
C34    1  0.00000  1.62538 -1.93303    0.05480  0.02365  0.01689

 * Atom defining the asymmetric unit for the found symmetry group


 Average difference on x,y,z,d   0.03062   0.04048   0.02445   0.06539

 Maximum difference on x,y,z,d   0.08578   0.20138   0.09778   0.21060
              due to the atoms    O13       O11       O33       O11

 Bond lengths and bond angles after symmetrization

RU1   -RU2    2.8420      RU1   -RU3    2.8420      RU1   -C11    1.9331
RU1   -C12    1.9135      RU1   -C13    1.9135      RU1   -C14    1.9331
O11   -C11    1.1305      O12   -C12    1.1261      C11   -RU1    1.9331
C11   -O11    1.1305      C12   -RU1    1.9135      C12   -O12    1.1261

RU2   -RU1   -RU3     60.000       RU2   -RU1   -C11     89.603
```

```
RU2   -RU1   -C12    157.965       RU2   -RU1   -C13     97.965
RU2   -RU1   -C14     89.603       RU3   -RU1   -C11     89.603
RU3   -RU1   -C12     97.965       RU3   -RU1   -C13    157.965
RU3   -RU1   -C14     89.603       C11   -RU1   -C12     90.282
C11   -RU1   -C13     90.282       C11   -RU1   -C14    179.083
C12   -RU1   -C13    104.070       C12   -RU1   -C14     90.282
C13   -RU1   -C14     90.282       RU1   -C11   -O11    172.943
RU1   -C12   -O12    179.971
```

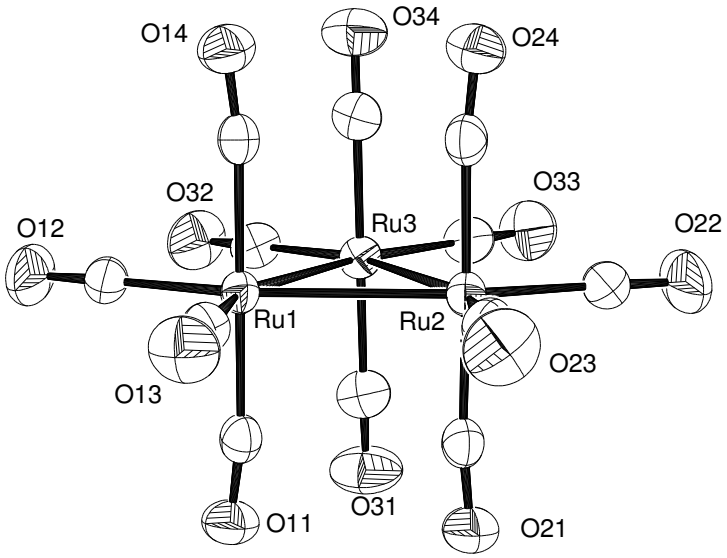
Symmetrised fractional coordinates

```
 RU1    1  0.80446  0.08032  0.66189  0.00003  0.00001  0.00001
 RU2    1  1.05705 -0.02256  0.77724  0.00003  0.00001  0.00001
 RU3    1  1.05833  0.16840  0.79155  0.00003  0.00001  0.00002
 O11    1  1.01274  0.09251  0.50752  0.00028  0.00017  0.00015
 O12    1  0.61312  0.24694  0.58086  0.00032  0.00018  0.00019
 O13    1  0.61096 -0.07504  0.55674  0.00032  0.00016  0.00017
 O14    1  0.57264  0.06882  0.80487  0.00028  0.00016  0.00017
 O21    1  1.28294 -0.01755  0.63091  0.00030  0.00019  0.00016
 O22    1  1.36655 -0.05995  0.92494  0.00032  0.00023  0.00019
 O23    1  0.93850 -0.20846  0.70632  0.00035  0.00017  0.00019
 O24    1  0.84283 -0.04124  0.92826  0.00031  0.00017  0.00016
 O31    1  1.28431  0.18673  0.64622  0.00034  0.00022  0.00020
 O32    1  0.94233  0.36115  0.74900  0.00035  0.00017  0.00021
 O33    1  1.36822  0.18768  0.94349  0.00032  0.00022  0.00018
 O34    1  0.84421  0.16304  0.94357  0.00032  0.00018  0.00017
 C11    1  0.94525  0.08777  0.56862  0.00035  0.00019  0.00020
 C12    1  0.68404  0.18522  0.61090  0.00035  0.00021  0.00020
 C13    1  0.68268 -0.01750  0.59571  0.00035  0.00021  0.00019
 C14    1  0.66687  0.07278  0.75670  0.00035  0.00018  0.00020
 C21    1  1.19545 -0.01414  0.68288  0.00037  0.00021  0.00020
 C22    1  1.25189 -0.04608  0.87022  0.00040  0.00024  0.00022
 C23    1  0.98239 -0.13958  0.73258  0.00039  0.00021  0.00022
 C24    1  0.91707 -0.02913  0.87096  0.00037  0.00019  0.00021
 C31    1  1.19672  0.17501  0.69705  0.00040  0.00022  0.00023
 C32    1  0.98527  0.28973  0.76475  0.00040  0.00022  0.00023
 C33    1  1.25341  0.18051  0.88720  0.00040  0.00023  0.00023
 C34    1  0.91834  0.16003  0.88513  0.00038  0.00020  0.00021
```

```
 Schoenflies symbol = D3h     CSM =  0.6444     Molecular RMS =  0.0803
 For the definition of Continuous Symmetry Measure (CSM), see:
 Zabrodsky et al. (1993) J.Am.Chem.Soc, 115, 8278-8298

 Symmetry group matrices


  1 CSM = 0.0000     Max. diff. (Angstrom)=0.0000     Type E
     1.0000000000    0.0000000000    0.0000000000
     0.0000000000    1.0000000000    0.0000000000
     0.0000000000    0.0000000000    1.0000000000


  2 CSM = 0.5832     Max. diff. (Angstrom)=0.1799     Type S3
    -0.5000000000    0.8660254038    0.0000000000
    -0.8660254038   -0.5000000000    0.0000000000
     0.0000000000    0.0000000000   -1.0000000000


  3 CSM = 0.4113     Max. diff. (Angstrom)=0.1201     Type C3
    -0.5000000000   -0.8660254038    0.0000000000
     0.8660254038   -0.5000000000    0.0000000000
     0.0000000000    0.0000000000    1.0000000000


  4 CSM = 0.3620     Max. diff. (Angstrom)=0.1228     Type Cs
     1.0000000000    0.0000000000    0.0000000000
```

```
     0.0000000000    1.0000000000    0.0000000000
     0.0000000000    0.0000000000   -1.0000000000


  5 CSM = 0.2767     Max. diff. (Angstrom)=0.1082     Type C2
    -1.0000000000    0.0000000000    0.0000000000
     0.0000000000    1.0000000000    0.0000000000
     0.0000000000    0.0000000000   -1.0000000000


  6 CSM = 0.4113     Max. diff. (Angstrom)=0.1201     Type C3
    -0.5000000000    0.8660254038    0.0000000000
    -0.8660254038   -0.5000000000    0.0000000000
     0.0000000000    0.0000000000    1.0000000000


  7 CSM = 0.5814     Max. diff. (Angstrom)=0.1543     Type Cs
     0.5000000000    0.8660254038    0.0000000000
     0.8660254038   -0.5000000000    0.0000000000
     0.0000000000    0.0000000000    1.0000000000


  8 CSM = 0.5832     Max. diff. (Angstrom)=0.1799     Type S3
    -0.5000000000   -0.8660254038    0.0000000000
     0.8660254038   -0.5000000000    0.0000000000
     0.0000000000    0.0000000000   -1.0000000000


  9 CSM = 0.2791     Max. diff. (Angstrom)=0.1003     Type C2
     0.5000000000   -0.8660254038    0.0000000000
    -0.8660254038   -0.5000000000    0.0000000000
     0.0000000000    0.0000000000   -1.0000000000


 10 CSM = 0.2923     Max. diff. (Angstrom)=0.1072     Type Cs
    -1.0000000000    0.0000000000    0.0000000000
     0.0000000000    1.0000000000    0.0000000000
     0.0000000000    0.0000000000    1.0000000000


 11 CSM = 0.2658     Max. diff. (Angstrom)=0.0985     Type C2
     0.5000000000    0.8660254038    0.0000000000
     0.8660254038   -0.5000000000    0.0000000000
     0.0000000000    0.0000000000   -1.0000000000


 12 CSM = 0.4216     Max. diff. (Angstrom)=0.2053     Type Cs
     0.5000000000   -0.8660254038    0.0000000000
    -0.8660254038   -0.5000000000    0.0000000000
     0.0000000000    0.0000000000    1.0000000000

  Symmetry operations in hexagonal coordinates

 Symmetry element its CSM and Max.Diff.   Symmetry element its CSM and
Max.Diff.
  1) [E  ]  x,y,z         0.0000  0.0000     2) [S3 ]  -x+y,-x,-z   0.5832
0.1799
  3) [C3 ]  -y,x-y,z      0.4113  0.1201     4) [Cs ]  x,y,-z       0.3620
0.1228
  5) [C2 ]  -x+y,y,-z     0.2767  0.1082     6) [C3 ]  -x+y,-x,z    0.4113
0.1201
  7) [Cs ]  x,x-y,z       0.5814  0.1543     8) [S3 ]  -y,x-y,-z    0.5832
0.1799
  9) [C2 ]  -y,-x,-z      0.2791  0.1003    10) [Cs ]  -x+y,y,z     0.2923
0.1072
```

```
 11) [C2 ]   x,x-y,-z      0.2658   0.0985    12) [Cs ]   -y,-x,z       0.4216
0.2053

 Oblique coordinates (hexagonal system)
   RU1       0.94734  -0.94734   0.00000
   RU2      -1.89468  -0.94734   0.00000
   RU3       0.94734   1.89468   0.00000
   O11       1.01341  -1.01341   3.05603
   O12       4.42322   0.36885   0.00000
   O13      -0.36885  -4.42322   0.00000
   O14       1.01341  -1.01341  -3.05603
   O21      -2.02683  -1.01341   3.05603
   O22      -4.05437   0.36885   0.00000
   O23      -4.05437  -4.42322   0.00000
   O24      -2.02683  -1.01341  -3.05603
   O31       1.01341   2.02683   3.05603
   O32       4.42322   4.05437   0.00000
   O33      -0.36885   4.05437   0.00000
   O34       1.01341   2.02683  -3.05603
   C11       0.93842  -0.93842   1.93303
   C12       3.13550  -0.11841   0.00000
   C13       0.11841  -3.13550   0.00000
   C14       0.93842  -0.93842  -1.93303
   C21      -1.87683  -0.93842   1.93303
   C22      -3.25391  -0.11841   0.00000
   C23      -3.25391  -3.13550   0.00000
   C24      -1.87683  -0.93842  -1.93303
   C31       0.93842   1.87683   1.93303
   C32       3.13550   3.25391   0.00000
   C33       0.11841   3.25391   0.00000
   C34       0.93842   1.87683  -1.93303
```



Atomic labelling scheme for $Ru_3(CO)_{12}$

References

1. T. Pilati & A. Forni (2000) *J. Appl. Cryst* **33**, 417-418