Supporting Information for

Comprehensive Solid State NMR Characterization of Electronic Structure in Ditechnetium Heptoxide

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Experimental

Caution. Technetium-99 is a beta-emitter with a specific activity of 629 MBq/g (E_{max} = 292 keV). All samples were prepared at the University of Nevada, Las Vegas in a laboratory designed for low level radioactivity using efficient HEPA-filtered fume hoods. Personal protective equipment was worn by workers at all times. NMR experiments were performed by radiologically-trained personnel in the Radiochemical Processing Laboratory, a Category 2 nuclear research facility at the Pacific Northwest National Laboratory.

Ammonium pertechnetate was purchased from Oak Ridge National Laboratory and purified according to a published procedure.[1] Oxygen-17 enriched water (20% enrichment, Los Alamos National Laboratory stock) was used for the preparation of labeled NH_4TcO_4*. Diechnetium heptoxide is a very hygroscopic and moderately volatile compound. To avoid exposure of the heptoxide to atmospheric moisture and minimize handling, it was synthesized in a specially designed Pyrex reactor (Figure S1). The synthesis of labeled Tc_2O_7 was accomplished in three steps: (1) synthesis of enriched NH_4TcO_4*, (2) synthesis of TcO_2* from NH_4TcO_4*, and (3) synthesis of Tc_2O_7* from TcO_2* followed by encapsulation in a 3 mm NMR tube.

Preparation of NH_4TcO_4.* The synthesis was modeled after the procedure of Jurisson and Murmann.[2] Ammonium pertechnetate (577 mg) was placed in a 25 ml round bottom flask holding a small stir bar. Enriched H_2O* (1.960 ml) and 0.1 M H_2SO_4 (40 μl) were added to the flask. The flask was closed with a rubber stopper and the suspension was stirred for 24 hours. The acidic solution was then neutralized with 1 M NH_4OH. The solution was frozen and pumped to dryness; the labeled water was recovered in a liquid N_2-cooled trap.

The resulting white solid (NH_4TcO_4*, 557 mg) was removed from the flask using a spatula.

Preparation of TcO_2.* A portion of the enriched ammonium pertechnetate (512 mg) was evenly dispersed in the bottom of an 8 cm quartz boat, which was placed in a 50 cm long 30 mm OD quartz tube stoppered at both ends with 25 mm quartz Solv-Seals. The tube was placed in a tube furnace (Barnstead Thermolyne, model 2100) so that the quartz boat was centered in the furnace. Solv-Seal end caps fitted with 15 mm greaseless stopcocks were attached and the apparatus was purged with argon for 30 minutes. The temperature was slowly raised to 700 °C and held there for 2 hours. After cooling to room temperature, black TcO_2* (355.2 mg) was obtained.[3]

Preparation and encapsulation of Tc_2O_7.* Labeled TcO_2 (160 mg) was placed at the sealed end of the reactor (Figure S1). The tube was connected to a Schlenk line via flexible rubber tubing, evacuated, and flamed carefully under vacuum to remove residual moisture from the TcO_2* and the Pyrex tube. After flaming, the tube was backfilled with dry oxygen gas, and subjected to two additional evacuate/backfill cycles and placed in the furnace. The temperature was raised to 500 °C and held for 2 hours under a static oxygen atmosphere. A yellow solid (Tc_2O_7*) and a red film were observed at the cold part of the tube just outside the furnace. After cooling to room temperature, the tube was removed from the furnace, evacuated to remove the red film (considerably more volatile than Tc_2O_7) and sealed under vacuum. The tube was clamped and tilted slightly toward the attached NMR tube. Ditechnetium heptoxide was carefully melted using a small hand-held butane torch (Blazer piezo micro torch, USP 4597732) and the yellow liquid was moved by gravity to the 3 mm OD NMR tube. After cooling, the protecting outer (length = 7 cm, OD

= 10 mm) glass tube, which was filled with helium, was carefully removed and the 3 mm NMR tube flame sealed. The resulting NMR tube (length ~2.8 mm) containing Tc_2O_7* (~100 mg) was checked for external contamination, and placed in a zirconia sleeve (5 mm OD) that was then capped at both ends with vespel plugs. The final ^{17}O enrichment is unknown, but estimated at 2-3%.

NMR spectroscopy. All NMR experiments were performed in a 7.04 Tesla magnet (Oxford Instruments, Inc.) with a Tecmag Discovery console and a 5 mm Chemagnetics HX solids probe. Technetium-99 spectra were acquired with a Hahn echo sequence (200 μs refocusing time)[4] using soft radiofrequency pulses (B_1 = 0.95 mT in the rotating frame) in order to ensure selective excitation of the +½↔-½ transition; the selectivity of the radiofrequency (rf) field was confirmed by comparison of nutation spectra for Tc_2O_7(s) and TcO_4^-(aq) samples, which revealed a clearly dominant $5\gamma B_1$ harmonic for the former.[5] An optimized two-pulse echo (148 μs refocusing time) with B_1 = 10.8 mT was used for detection of the ^{17}O resonance. Spin-lattice relaxation times measured by the saturation recovery method were 0.63 and 10-20 s for ^{99}Tc and ^{17}O, respectively. Signal averages typically involved 12800 scans at 5 s/scan for ^{99}Tc spectra and 4096 scans at 60 s/scan for ^{17}O spectra.

Computational Details

The definition and sign of the shielding in relation to the chemical shift conform to the IUPAC recommendation.[6] Chemical shift tensor principal values were defined and ordered according to the convention of Haeberlen.[7] Electric field gradient principal values and the parameters V_{zz} and η_Q follow the definitions of Cohen and Reif.[8]

The modeled system was a cluster of 17 molecules (153 atoms; Figure S2) based on the structure data of Krebs.[9] NMR properties were calculated for the central molecule of the cluster.

References

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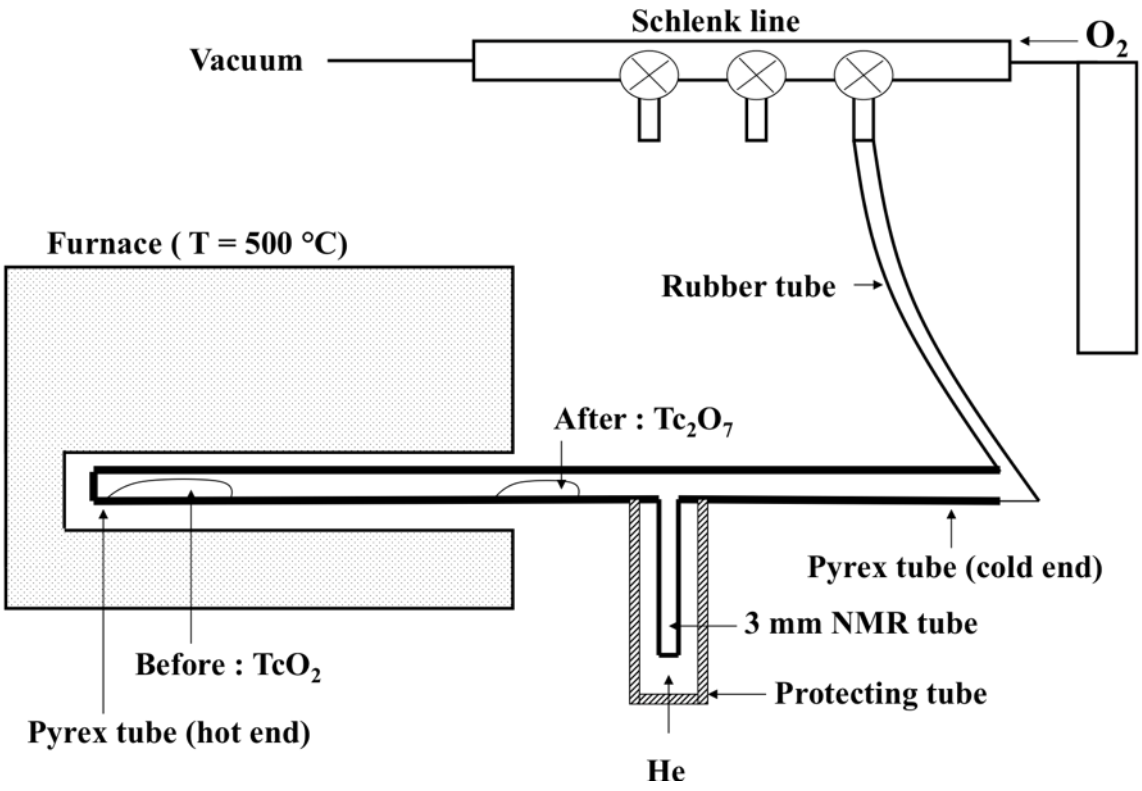

Figure S1: Apparatus for converting TcO_2 to Tc_2O_7, and collecting in the NMR tube.

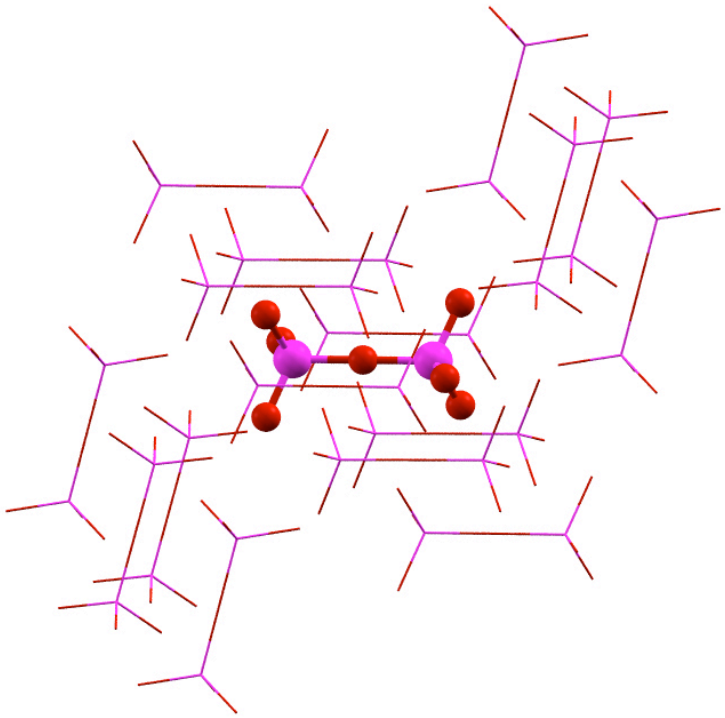

Figure S2: The $(Tc_2O_7)_{17}$ cluster used for calculation of NMR parameters. Data in Table 1 pertain to the central highlighted molecule (Tc in purple, O in red).

APPENDIX SA

Atomic Coordinates Used in Computations

Cartesian coordinates (in Å) below specify a $(Tc_2O_7)_{17}$ cluster, and are based on the structure of Krebs, B. *Zeit. Anorg. Allg. Chem.* **1971,** 146-159 (Figure S2). First nine atoms are the centrosymmetric central Tc_2O_7, for which NMR parameters were calculated:

O	0.0000	0.0000	0.0000	(Bridge)
O	-1.6405	1.6482	-1.6749	(Terminal 1)
O	1.6405	-1.6482	1.6749	(Terminal 1')
O	-0.3233	-0.4368	-2.8452	(Terminal 2)
O	0.3233	0.4368	2.8452	(Terminal 2')
O	-2.4372	-0.9070	-1.1843	(Terminal 3)
O	2.4372	0.9071	1.1843	(Terminal 3')
Tc	-1.1056	0.1020	-1.4677	
Tc	1.1056	-0.1020	1.4677	
O	-2.8030	3.7236	-0.0207	
O	-2.7643	-0.0009	-6.8959	
O	-5.6169	0.0082	-0.0360	
O	-2.8139	-3.7154	-0.0154	
O	-2.8526	0.0091	6.8598	
O	0.0496	3.7145	-6.8805	
O	0.0110	7.4390	-0.0053	
O	2.8139	3.7154	0.0154	
O	-0.0387	3.7245	6.8752	
O	2.8526	-0.0091	-6.8598	
O	0.0387	-3.7245	-6.8752	
O	2.8030	-3.7236	0.0207	
O	2.7643	0.0009	6.8959	
O	-0.0496	-3.7145	6.8805	
O	-0.0110	-7.4390	0.0053	
O	5.6169	-0.0082	0.0360	
O	-7.2574	1.6564	-1.7109	
O	-1.6295	9.0872	-1.6802	
O	-4.4483	2.0778	-1.6932	
O	-1.6122	5.3651	-5.2292	
O	-1.0976	1.6425	-8.5495	
O	-1.1576	5.3694	1.6518	
O	-1.7005	5.3751	8.5264	
O	-1.1859	1.6525	5.2062	
O	-1.6515	-5.7908	-1.6695	
O	-4.4593	-5.3612	-1.6878	
O	-4.4310	-1.6443	-5.2422	
O	-1.6232	-2.0739	-5.2239	
O	-3.9764	-1.6400	1.6388	
O	-1.1686	-2.0696	1.6571	
O	-4.5193	-1.6342	8.5134	
O	-1.7115	-2.0639	8.5318	
O	3.9764	1.6400	-1.6388	
O	1.1685	2.0696	-1.6571	
O	4.5193	1.6342	-8.5135	
O	1.7115	2.0639	-8.5318	
O	1.6515	5.7908	1.6695	

O	4.4593	5.3612	1.6878
O	4.4310	1.6442	5.2422
O	1.6232	2.0739	5.2239
O	1.1576	-5.3694	-1.6518
O	1.1859	-1.6525	-5.2062
O	1.7005	-5.3751	-8.5264
O	4.4483	-2.0778	1.6932
O	1.0976	-1.6425	8.5495
O	1.6122	-5.3651	5.2292
O	1.6295	-9.0872	1.6802
O	7.2574	-1.6564	1.7109
O	-5.9402	-0.4285	-2.8812
O	-0.3124	7.0022	-2.8505
O	-3.1250	4.1572	-2.8665
O	-3.1228	0.4369	-4.0551
O	-0.3102	3.2819	-4.0391
O	-5.2935	0.4450	2.8091
O	-2.4809	3.2900	2.8251
O	-3.2111	0.4469	9.7006
O	-0.3985	3.2919	9.7166
O	-3.1360	-3.2818	-2.8611
O	-0.3212	-4.1571	-4.0337
O	-2.4057	-0.4386	-9.7367
O	-2.4919	-4.1490	2.8304
O	-0.4095	-4.1471	9.7219
O	-2.4940	-0.4286	4.0190
O	-0.3343	-7.8757	-2.8398
O	0.3343	7.8757	2.8398
O	2.4919	4.1490	-2.8304
O	2.4940	0.4286	-4.0190
O	0.4095	4.1471	-9.7219
O	3.1360	3.2818	2.8611
O	2.4057	0.4386	9.7366
O	0.3212	4.1571	4.0337
O	5.2935	-0.4450	-2.8091
O	2.4809	-3.2900	-2.8251
O	3.2111	-0.4469	-9.7006
O	0.3985	-3.2919	-9.7166
O	0.3124	-7.0022	2.8505
O	3.1250	-4.1572	2.8665
O	3.1228	-0.4369	4.0551
O	0.3102	-3.2819	4.0391
O	5.9402	0.4285	2.8812
O	-8.0540	-0.8988	-1.2203
O	-2.4262	6.5319	-1.1896
O	-5.2374	4.6361	-1.2063
O	-5.2138	0.9133	-5.7430
O	-2.4025	2.8091	-5.7263
O	-3.1797	0.9153	1.1482
O	-0.3685	2.8111	1.1649
O	-5.3021	0.9233	8.0127
O	-2.4909	2.8192	8.0294
O	-5.2484	-2.8029	-1.2009
O	-2.4135	-4.6299	-5.7210
O	-0.3148	-0.9151	-8.0488

O	-0.3794	-4.6279	1.1702
O	-2.5018	-4.6198	8.0347
O	-0.4031	-0.9051	5.7069
O	-2.4481	-8.3461	-1.1789
O	2.4481	8.3460	1.1789
O	0.3794	4.6279	-1.1702
O	0.4031	0.9051	-5.7069
O	2.5018	4.6198	-8.0347
O	5.2484	2.8029	1.2009
O	0.3148	0.9151	8.0488
O	2.4135	4.6299	5.7210
O	3.1797	-0.9153	-1.1482
O	0.3685	-2.8111	-1.1649
O	5.3021	-0.9234	-8.0127
O	2.4909	-2.8191	-8.0294
O	2.4262	-6.5319	1.1896
O	5.2374	-4.6361	1.2063
O	5.2138	-0.9133	5.7430
O	2.4025	-2.8091	5.7263
O	8.0540	0.8988	1.2203
Tc	-6.7225	0.1103	-1.5037
Tc	-1.0946	7.5410	-1.4730
Tc	-3.9088	3.6227	-1.4882
Tc	-1.0747	3.8186	-5.4273
Tc	-1.6396	0.0979	-8.3492
Tc	-1.6971	3.8245	1.4468
Tc	-1.1630	3.8287	8.3284
Tc	-1.7280	0.1079	5.4064
Tc	-1.1165	-7.3370	-1.4623
Tc	-3.9198	-3.8163	-1.4829
Tc	-3.8889	-0.0997	-5.4425
Tc	-1.0857	-3.6203	-5.4219
Tc	-4.5113	-0.0938	1.4316
Tc	-1.7080	-3.6145	1.4522
Tc	-3.9772	-0.0896	8.3132
Tc	-1.1740	-3.6103	8.3337
Tc	4.5113	0.0938	-1.4316
Tc	1.7080	3.6145	-1.4522
Tc	3.9772	0.0896	-8.3132
Tc	1.1740	3.6103	-8.3337
Tc	1.1165	7.3370	1.4623
Tc	3.9198	3.8163	1.4829
Tc	3.8889	0.0997	5.4425
Tc	1.0857	3.6203	5.4220
Tc	1.6971	-3.8245	-1.4468
Tc	1.7280	-0.1079	-5.4064
Tc	1.1630	-3.8287	-8.3284
Tc	3.9088	-3.6227	1.4882
Tc	1.6396	-0.0979	8.3492
Tc	1.0747	-3.8186	5.4273
Tc	1.0946	-7.5410	1.4730
Tc	6.7225	-0.1103	1.5037

Oxygen atom	Tc-O distance (Å)
Bridge	1.840
Terminal 1, 1′	1.649
Terminal 2, 2′	1.673
Terminal 3, 3′	1.695

Reference isotropic shielding for Technetium and Oxygen with solvent corrections

Tc from TcO4- : -1287.80 ppm
O from H2O : 242.97 ppm

Shielding and electric field gradient tensor data

Bridge Oxygen:

```
 ===== principal axes Q-tensor (EFG)
           11            22            33
    X   -0.162462      0.786940      0.595258
    Y    0.966221      0.249192     -0.065728
    Z    0.200058     -0.564472      0.800842
 ==== principal values EFG
 O  EFG -0.544318E+00 -0.515879E+00  0.106020E+01  a.u.
 ==== principal values Q-tensor (multiplied by Q (e 10-24 cm2) /
2I(2I-1))
          q11           q22           q33
         0.163578E+00  0.155032E+00 -0.318610E+00  MHz
         0.545639E-01  0.517131E-01 -0.106277E+00  10-4 cm-1

 17. O   NQCC = -0.637221E+01 MHz,    eta =  0.02682

=== SCALED: TOTAL NMR SHIELDING TENSOR (ppm)

                        **********************************
                        CARTESIAN AXIS REPRESENTATION

                        ==== total shielding tensor
                        ----------------------------------
                              -2.998    18.205   -70.357
                              18.205    57.462   -10.673
                             -70.357   -10.673   -39.062
                        ----------------------------------
                        isotropic shielding =      5.134

                        **********************************
                        ----------------------------------
                        PRINCIPAL AXIS REPRESENTATION

                        ==== Shieldings:

                             -93.710    33.427    75.686

                        ==== Principal Axis System:

                               0.615     0.588    -0.526
                              -0.018    -0.656    -0.755
                               0.788    -0.474     0.392
                        ----------------------------------
```

Terminal Oxygen 1 (Tc-O bond length = 1.649 Å):

```
 ===== principal axes Q-tensor (EFG)
           11            22            33
    X   -0.692706      0.642226     -0.328183
    Y   -0.248392     -0.639641     -0.727434
    Z    0.677097      0.422380     -0.602607
 ==== principal values EFG
 O  EFG -0.474285E+00  0.401736E-01  0.434111E+00  a.u.
 ==== principal values Q-tensor (multiplied by Q (e 10-24 cm2) /
2I(2I-1))
          q11           q22           q33
         0.142532E+00 -0.120730E-01 -0.130459E+00  MHz
         0.475436E-01 -0.402711E-02 -0.435165E-01  10-4 cm-1

 17. O   NQCC =  0.285064E+01 MHz,    eta =  0.83059

=== SCALED: TOTAL NMR SHIELDING TENSOR (ppm)

                        **********************************
                        CARTESIAN AXIS REPRESENTATION

                        ==== total shielding tensor
                        ----------------------------------
                            -776.954   -41.483   291.584
                             -41.483  -562.893    64.919
                             291.584    64.919  -696.254
                        ----------------------------------
                        isotropic shielding =   -678.700

                        **********************************
                        ----------------------------------
                        PRINCIPAL AXIS REPRESENTATION

                        ==== Shieldings:

                           -1042.381  -555.556  -438.164

                        ==== Principal Axis System:

                              -0.742     0.236     0.628
                              -0.153    -0.971     0.185
                               0.653     0.041     0.756
                        ----------------------------------
```

Terminal Oxygen 2 (Tc-O bond length = 1.673 Å):

```
 ===== principal axes Q-tensor (EFG)
           11            22            33
    X   -0.284094      0.055075      0.957213
    Y   -0.913055      0.289142     -0.287624
    Z    0.292612      0.955701      0.031857
 ==== principal values EFG
 O  EFG -0.542206E+00  0.742634E-01  0.467943E+00  a.u.
 ==== principal values Q-tensor (multiplied by Q (e 10-24 cm2) /
2I(2I-1))
          q11           q22           q33
         0.162944E+00 -0.223176E-01 -0.140626E+00  MHz
         0.543522E-01 -0.744436E-02 -0.469079E-01  10-4 cm-1

 17. O   NQCC =  0.325888E+01 MHz,    eta =  0.72607

=== SCALED: TOTAL NMR SHIELDING TENSOR (ppm)

                        **********************************
                        CARTESIAN AXIS REPRESENTATION

                        ==== total shielding tensor
                        ----------------------------------
                            -551.353  -143.339    97.719
                            -143.339 -1050.324   111.092
                              97.719   111.092  -596.109
                        ----------------------------------
                        isotropic shielding =   -732.596

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                        PRINCIPAL AXIS REPRESENTATION

                        ==== Shieldings:

                           -1122.399  -606.184  -469.204

                        ==== Principal Axis System:

                              -0.275    -0.488     0.828
                              -0.929     0.357    -0.099
                               0.247     0.797     0.551
                        ----------------------------------
```

Terminal Oxygen 3 (Tc-O bond length = 1.695 Å):

```
 ===== principal axes Q-tensor (EFG)
           11            22            33
    X    0.506603      0.856657     -0.097425
    Y   -0.751850      0.383640     -0.536229
    Z   -0.421988      0.344905      0.838431
 ==== principal values EFG
 O  EFG -0.571702E+00  0.964355E-01  0.475267E+00  a.u.
 ==== principal values Q-tensor (multiplied by Q (e 10-24 cm2) /
2I(2I-1))
          q11           q22           q33
         0.171808E+00 -0.289808E-01 -0.142827E+00  MHz
         0.573090E-01 -0.966695E-02 -0.476420E-01  10-4 cm-1

 17. O   NQCC =  0.343616E+01 MHz,    eta =  0.66264

=== SCALED: TOTAL NMR SHIELDING TENSOR (ppm)

                        **********************************
                        CARTESIAN AXIS REPRESENTATION

                        ==== total shielding tensor
                        ----------------------------------
                            -694.015   167.892   174.290
                             167.892  -872.810  -204.761
                             174.290  -204.761  -519.884
                        ----------------------------------
                        isotropic shielding =   -695.570

                        **********************************
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                        PRINCIPAL AXIS REPRESENTATION

                        ==== Shieldings:

                           -1096.480  -600.403  -389.825

                        ==== Principal Axis System:

                               0.498     0.782     0.375
                              -0.759     0.602    -0.248
                              -0.420    -0.160     0.893
                        ----------------------------------
```

Technetium:

```
 ===== principal axes Q-tensor (EFG)
           11            22            33
    X    0.442376     -0.062543      0.894646
    Y   -0.713861     -0.628402      0.309052
    Z   -0.542868      0.775371      0.322637
 ==== principal values EFG
 Tc EFG -0.269675E+00 -0.119653E-01  0.281640E+00  a.u.
 ==== principal values Q-tensor (multiplied by Q (e 10-24 cm2) /
2I(2I-1))
          q11           q22           q33
         0.113527E+00  0.503714E-02 -0.118565E+00  MHz
         0.378687E-01  0.168021E-02 -0.395489E-01  10-4 cm-1

 99. Tc  NQCC = -0.853665E+01 MHz,    eta =  0.91503

=== SCALED: TOTAL NMR SHIELDING TENSOR (ppm)

                        **********************************
                        CARTESIAN AXIS REPRESENTATION

                        ==== total shielding tensor
                        ----------------------------------
                           -1252.992    51.360   226.580
                              51.360 -1606.443    17.982
                             226.580    17.982 -1220.567
                        ----------------------------------
                        isotropic shielding =  -1360.001

                        **********************************
                        ----------------------------------
                        PRINCIPAL AXIS REPRESENTATION

                        ==== Shieldings:

                           -1614.540 -1459.712 -1005.749

                        ==== Principal Axis System:

                               0.174    -0.710     0.682
                              -0.983    -0.165     0.080
                              -0.055     0.685     0.727
                        ----------------------------------
```