Supplementary Materials

Polymerisation Isomerism of Tungsten(VI) Oxomethoxide: New Insights into Structure and Reactivity of Non-Cluster Metal Oxoalkoxide Aggregates

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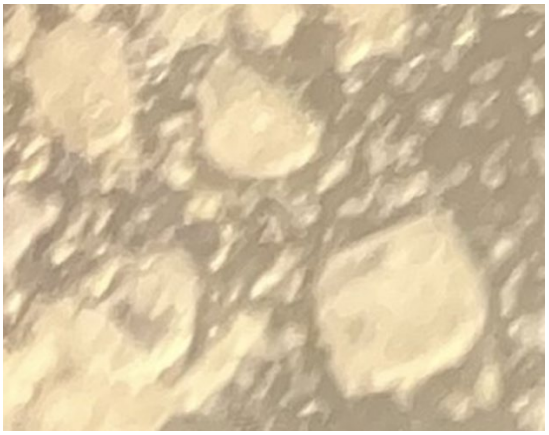

Figure S1. Optical microscopy view of the crystals of 2 freshly separated from methanol at – 18°C

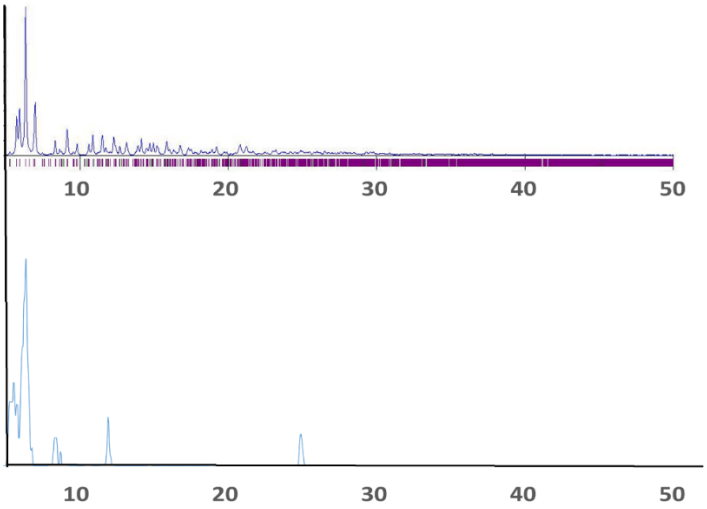

Figure S2. X-ray powder pattern of compound 2 – experimental (below) and obtained by theoretical calculation from single crystal data using CCDC Mercury program (above).

Figure S3. Optical microscopy view of the product of storage of the crystals of **2** under minimal amount of methanol overnight.

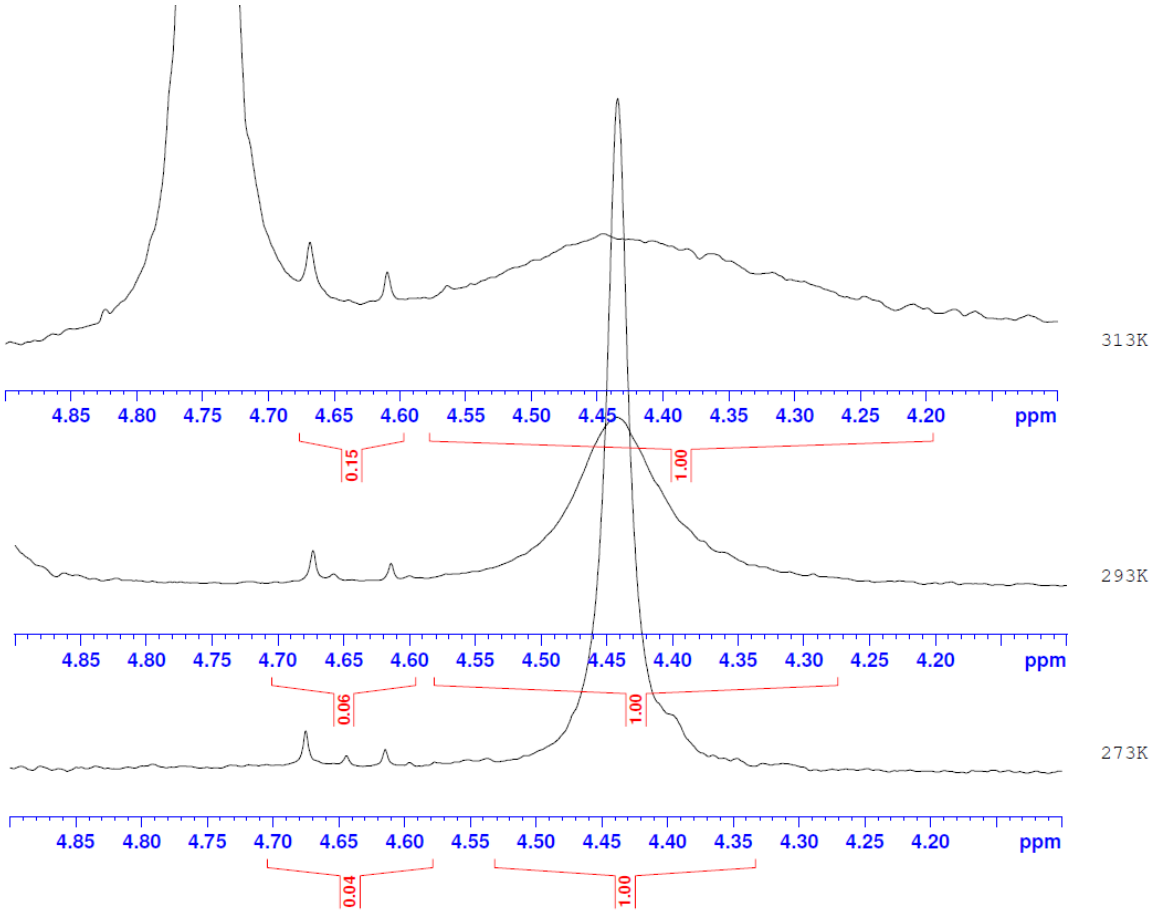

Figure S4. Integration of the spectra of $WO(OMe)_4$ in methanol.

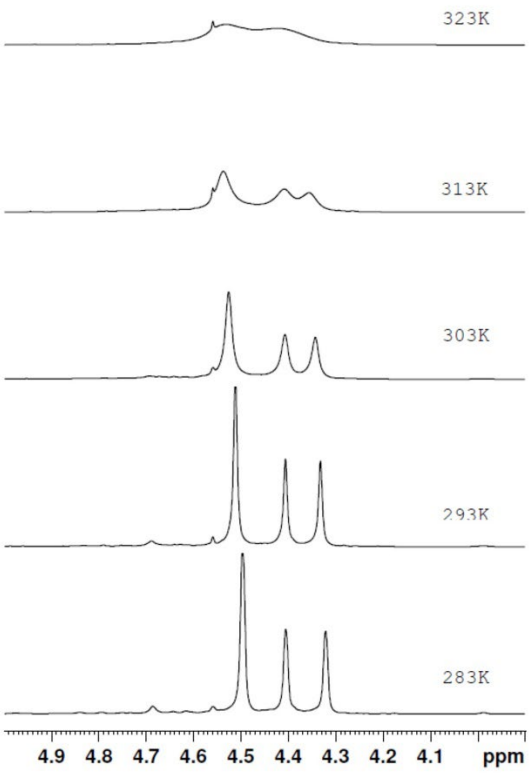

Figure S5. ^{1}H NMR spectrum of $WO(OMe)_4$ in C_6D_6 at selected temperatures.

Structural models and computational details

All computations were performed using the program Crystal 23.[1] Visualizations and structural modifications were made using the Cambridge Crystallographic Data Centre program Mercury [2] Density functional theory (DFT) computations were performed using the hybrid density functional cam-B3LYP including long-range corrections,[3] and the basis set for W was based on the Stuttgart-Dresden-Cologne MDF60 effective-core potential (ECP) and a valence space of double-zeta quality.[4] The lighter elements were modelled using basis sets of 6-311G quality amended by polarization functions. [5]

The determined crystal structures of the dimeric and polymeric forms of $WO(OMe)_4$ contain features that render them unsuitable for direct computational modelling. First, they lack the methyl-group hydrogen atoms, and second, they contain positional disorder generated by the space-group symmetry elements. Therefore, the following procedures were performed to generate suitable structural models based on the determined crystal structures. In the dimeric structure, the methyl-group hydrogen atoms were introduced using a riding model, packing was generated using the initial space group $P2_1/c$ (No. 14) and subsequently the symmetry was reduced in steps to P1 (No. 1). This removed a positional disorder in some of the methoxy hydrogen atoms. In the polymeric structure, determined in the space group Pmmm (No. 47), the same procedure was applied to generate the structure in the P1 space group. This removed a disorder of the methoxy groups. However, a positional disorder of the bridging oxygen atoms of the W=O entity remained. One of these two equivalent positions was removed to generate a chain with molecular $WO(OMe)_4$ building blocks, with one short, intra-molecular, W-O contact (1.816 Å; to be compared to the corresponding distance in the dimeric structure of 1.695 or 1.702 Å), and one long, inter-molecular, W-O contact

(2.175 Å). Of course, computations not exploiting the space-group symmetry will become more costly in time, but the systems are sufficiently small to allow such an approximation.

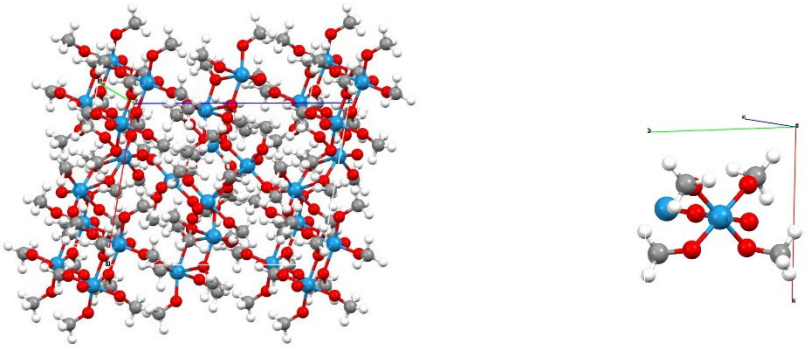

Figure S6. Unit cells of the structural models, dimeric structure to the left and the polymeric structure to the right, studied computationally in the formal space group P1.

References

1. Crystal 23: A. Erba, J. K. Desmarais, S. Casassa, B. Civalleri, L. Donà, I. J. Bush, B. Searle, L. Maschio, L.-E. Daga, A. Cossard, C. Ribaldone, E. Ascrizzi, N. L. Marana, J.-P. Flament, B. Kirtman, *J. Chem. Theory Comput.*, 2023, 19, 20, 6891–6932; R. Dovesi, V.R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N.M. Harrison, I.J. Bush, Ph. D'Arco, M. Llunell, M. Causà, Y. No&eul, L. Maschio, A. Erba, M. Rerat, S. Casassa, B.G. Searle, J.K. Desmarais, CRYSTAL23 User's Manual, University of Torino, Torino, 2023.
2. Mercury 4.0: C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler, P. A. Wood, *J. Appl. Cryst.*, 2020, *53*, 226-235.
3. T. Yanai, D. P. Tew, N. C. Handy, *Chem. Phys. Lett.*, 2004, *393*, 51-57.
4. D. Figgen, K. A. Peterson, M. Dolg, H. Stoll, *J. Chem. Phys.*, 2009, *130*, 164108.
5. C. Gatti, V. R. saunders, C. Roetti, *J. Chem. Phys.*, 1994, *101*, 10686-10696.

Crystal Structure Report for Compound 1

A specimen of $C_4H_{12}O_5W$, approximate dimensions 0.070 mm x 0.080 mm x 0.240 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å).

Table S1.1: Data collection details for WOMeNw_20250328.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA
Omega	59.362	69.63	-111.37	0.00	54.76	2.00	91	2.00	0.71076	50	20.0
Omega	59.362	46.42	-134.58	40.00	54.76	2.00	91	2.00	0.71076	50	20.0
Omega	59.362	46.42	-134.58	-120.00	54.76	2.00	91	2.00	0.71076	50	20.0
Omega	59.362	46.42	-134.58	80.00	54.76	2.00	91	2.00	0.71076	50	20.0
Omega	59.362	46.42	-134.58	0.00	54.76	2.00	91	2.00	0.71076	50	20.0
Omega	59.362	46.42	47.42	-40.00	54.76	2.00	91	2.00	0.71076	50	20.0
Omega	59.362	31.42	-149.58	0.00	54.76	2.00	91	2.00	0.71076	50	20.0

A total of 637 frames were collected. The total exposure time was 0.35 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a tetragonal unit cell yielded a total of 8375 reflections to a maximum θ angle of 39.46° (0.56 Å resolution), of which 1223 were independent (average redundancy 9.108, completeness = 99.0%, R_{int} = 4.20%, R_{sig} = 2.12%) and 1102 (90.00%) were greater than $2\sigma(F^2)$. The final cell constants of a = 7.1477(2) Å, b = 7.1477(2) Å, c = 4.0139(2) Å, volume = 205.069(15) $Å^3$, are based upon the refinement of the XYZ-centroids of 2595 reflections above 20 σ(I) with 11.41° < 2θ < 53.96°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.811. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.1330 and 0.4400.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -4, with Z = 1 for the formula unit, $C_4H_{12}O_5W$. The final anisotropic full-matrix least-squares refinement on F^2 with 30 variables converged at R1 = 3.16%, for the observed data and wR2 = 4.91% for all data. The goodness-of-fit was 1.035 The largest peak in the final difference electron density synthesis was 2.309 $e^-/Å^3$ and the largest hole was -1.798 $e^-/Å^3$ with an RMS deviation of 0.202 $e^-/Å^3$. On the basis of the final model, the calculated density was 2.623 g/cm^3 and F(000), 150 e^-.

Table S1.2. Sample and crystal data for Compound 1.

Identification code	WOMeNw_20250328

Chemical formula	$C_4H_{12}O_5W$	
Formula weight	323.99 g/mol	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal size	0.070 x 0.080 x 0.240 mm	
Crystal system	tetragonal	
Space group	P -4	
Unit cell dimensions	a = 7.1477(2) Å	α = 90°
	b = 7.1477(2) Å	β = 90°
	c = 4.0139(2) Å	γ = 90°
Volume	205.069(15) $Å^3$	
Z	1	
Density (calculated)	2.623 g/cm^3	
Absorption coefficient	14.052 mm^{-1}	
F(000)	150	

Table S1.3. Data collection and structure refinement for Compound 1

Theta range for data collection	5.71 to 39.46°	
Index ranges	-12<=h<=12, -12<=k<=12, -7<=l<=7	
Reflections collected	8375	
Independent reflections	1223 [R(int) = 0.0420]	
Coverage of independent reflections	99.0%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.4400 and 0.1330	
Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2018/2	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	1102 / 0 / 31	
Goodness-of-fit on F^2	1.035	
Final R indices	1102 data; I>2σ(I)	R1 = 0.0316, wR2 = 0.0491
	all data	R1 = 0.0400, wR2 = 0.0518
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0272P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.48(5	
Largest diff. peak and hole	2.309 and -1.798 $eÅ^{-3}$	
R.M.S. deviation from mean	0.202 $eÅ^{-3}$	

Table S1.4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for Compound 1

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
W1	0.500000	0.500000	0.000000	0.02565(10)
O2	0.500000	0.500000	0.500000	0.056(2)
O3	0.3180(9)	0.3141(9)	0.9336(15)	0.0360(15)
C1	0.1566(12)	0.3008(16)	0.729(2)	0.057(2)
O3A	0.2468(18)	0.4413(19)	0.931(3)	0.036(15)
C1A	0.1566(12)	0.3008(17)	0.729(2)	0.057(2)

Table S1.5. Bond lengths (Å) for Compound 1.

W1-O3A#2	1.879(13)	W1-O3A#3	1.879(13)
W1-O3A#4	1.879(12)	W1-O3A	1.879(12)
W1-O3	1.878(6)	W1-O3#2	1.878(6)
W1-O3#3	1.878(6)	W1-O3#4	1.878(6)
W1-O2#1	2.00695(10)	W1-O2	2.00695(10)
O3-C1	1.420(10)	O3A-C1A	1.443(15)

Symmetry transformations used to generate equivalent atoms:

#1 x, y, z+1

#2 -x+1, -y+1, z

#3 y, -x+1, -z+2

#4 -y+1, x, -z+2

Table S1.6. Bond angles (°) for Compound 1.

O3A#3-W1-O3A#4	91.28(13)	O3A#3-W1-O3A#5	91.28(13)
O3A#4-W1-O3A#5	162.8(9)	O3A#3-W1-O3A	162.8(9)
O3A#4-W1-O3A	91.28(13)	O3A#5-W1-O3A	91.28(13)
O3A#3-W1-O3#3	32.3(5)	O3A#4-W1-O3#3	59.6(5)
O3A#5-W1-O3#3	123.3(5)	O3A-W1-O3#3	143.4(5)
O3-W1-O3#3	163.7(4)	O3A#3-W1-O3#4	123.3(5)
O3A#4-W1-O3#4	32.3(5)	O3A#5-W1-O3#4	143.4(5)
O3A-W1-O3#4	59.6(5)	O3-W1-O3#4	91.16(6)
O3#3-W1-O3#4	91.16(6)	O3-W1-O3#5	91.16(6)

O3#3-W1-O3#5	91.16(6)	O3#4-W1-O3#5	163.7(4)
O3-W1-O2#2	98.2(2)	O3#3-W1-O2#2	98.2(2)
O3#4-W1-O2#2	81.8(2)	O3#5-W1-O2#2	81.8(2)
O3A#3-W1-O2	81.4(4)	O3A#4-W1-O2	98.6(4)
O3A#5-W1-O2	98.6(4)	O3A-W1-O2	81.4(4)
O3-W1-O2	81.8(2)	O3#3-W1-O2	81.8(2)
O3#4-W1-O2	98.2(2)	O3#5-W1-O2	98.2(2)
O2#2-W1-O2	180.000000	W1#1-O2-W1	180.000000
C1-O3-W1	133.8(7)	C1A-O3A-W1	132.2(11)

Symmetry transformations used to generate equivalent atoms:

#1 x, y, z-1

#2 x, y, z+1

#3 -x+1, -y+1, z

#4 y, -x+1, -z+2

#5 -y+1, x, -z+2

Table S1.7. Anisotropic atomic displacement parameters (Å^2) for Compound 1.

The anisotropic atomic displacement factor exponent takes the form:
$-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12} W1
	0.03246(13)	0.03246(13)	0.01204(12)	0.000000	0.000000	
O2	0.036(2)	0.036(2)	0.097(7)	0.000000	0.000000	0.000000
O3	0.040(3)	0.043(3)	0.026(4)	0.001(3)	-0.005(2)	-0.015(2)
C1	0.048(4)	0.082(6)	0.041(4)	0.002(4)	-0.008(3)	-0.018(5)
O3A	0.040(3)	0.043(3)	0.026(4)	0.001(3)	-0.005(2)	-0.015(2)
C1A	0.048(4)	0.082(6)	0.041(4)	0.002(4)	-0.008(3)	-0.018(5)

Table S1.8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for Compound 1.

	x/a	y/b	z/c	U(eq)
H1A	0.1373	0.1731	0.6649	0.086000
H1B	0.1729	0.3767	0.5342	0.086000
H1C	0.0494	0.3444	0.8517	0.086000
H1A1	0.0674	0.3596	0.5840	0.086000
H1A2	0.0930	0.2135	0.8717	0.086000
H1A3	0.2485	0.2362	0.5992	0.086000

Crystal Structure Report for Compound 2

A specimen of $C_8H_{24}O_{10}W_2$, approximate dimensions 0.160 mm x 0.200 mm x 0.240 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å).

Table S2.1: Data collection details for Compound 2.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA
Omega	59.385	-28.00	-28.00	0.00	54.76	0.30	606	5.00	0.71076	50	20.0
Omega	59.385	-28.00	-28.00	90.00	54.76	0.30	606	5.00	0.71076	50	20.0
Omega	59.385	-28.00	-28.00	180.00	54.76	0.30	606	5.00	0.71076	50	20.0
Omega	59.385	-28.00	-28.00	270.00	54.76	0.30	606	5.00	0.71076	50	20.0

A total of 2424 frames were collected. The total exposure time was 3.37 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 24514 reflections to a maximum θ angle of 28.00° (0.76 Å resolution), of which 3985 were independent (average redundancy 6.152, completeness = 98.6%, R_{int} = 5.54%, R_{sig} = 3.66%) and 3582 (89.89%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.4394(6) Å, b = 11.6788(7) Å, c = 13.8970(8) Å, β = 98.9000(10)°, volume = 1673.92(17) $Å^3$, are based upon the refinement of the XYZ-centroids of 9899 reflections above 20 σ(I) with 4.558° < 2θ < 67.96°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.236. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.1370 and 0.2170.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_8H_{24}O_{10}W_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 182 variables converged at R1 = 2.42%, for the observed data and wR2 = 5.55% for all data. The goodness-of-fit was 1.046. The largest peak in the final difference electron density synthesis was 1.133 $e^-/Å^3$ and the largest hole was -1.147 $e^-/Å^3$ with an RMS deviation of 0.139 $e^-/Å^3$. On the basis of the final model, the calculated density was 2.571 g/cm^3 and F(000), 1200 e^-.

Table S2.2. Sample and crystal data for Compound 2.

Identification code	WOMe_250319
Chemical formula	$C_8H_{24}O_{10}W_2$

Formula weight	647.97 g/mol	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal size	0.160 x 0.200 x 0.240 mm	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 10.4394(6) Å	α = 90°
	b = 11.6788(7) Å	β = 98.9000(10)°
	c = 13.8970(8) Å	γ = 90°
Volume	1673.92(17) $Å^3$	
Z	4	
Density (calculated)	2.571 g/cm^3	
Absorption coefficient	13.772 mm^{-1}	
F(000)	1200	

Table S2.3. Data collection and structure refinement for Compound 2.

Theta range for data collection	2.29 to 28.00°	
Index ranges	-13<=h<=13, -15<=k<=15, -18<=l<=18	
Reflections collected	24514	
Independent reflections	3985 [R(int) = 0.0554]	
Coverage of independent reflections	98.6%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.2170 and 0.1370	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014 (Sheldrick 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3985 / 0 / 182	
Goodness-of-fit on F^2	1.046	
Δ/σ_{max}	0.002	
Final R indices	3582 data; I>2σ(I)	R1 = 0.0242, wR2 = 0.0540
	all data	R1 = 0.0295, wR2 = 0.0555
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0139P)^2+3.9100P]$ where $P=(F_o^2+2F_c^2)/3$	
Extinction coefficient	0.0023(2)	
Largest diff. peak and hole	1.133 and -1.147 $eÅ^{-3}$	
R.M.S. deviation from mean	0.139 $eÅ^{-3}$	

Table S2.4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for Compound 2.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
W1	0.89187(2)	0.02537(2)	0.58298(2)	0.02917(7)
W2	0.61820(2)	0.56692(2)	0.44194(2)	0.03156(7)
O4	0.0352(3)	0.0970(2)	0.5193(2)	0.0312(7)
O14	0.4317(3)	0.5783(3)	0.4653(2)	0.0325(7)
O2	0.7673(3)	0.0622(3)	0.4738(3)	0.0447(8)
O11	0.5701(4)	0.4641(3)	0.3393(3)	0.0488(9)
O1	0.7751(3)	0.9159(3)	0.6186(3)	0.0473(9)
O5	0.8670(4)	0.1447(3)	0.6477(3)	0.0497(9)
O3	0.0154(3)	0.9552(3)	0.6761(3)	0.0408(8)
O13	0.6731(3)	0.6366(3)	0.5625(3)	0.0443(8)
O15	0.6087(4)	0.6871(3)	0.3717(3)	0.0512(9)
O12	0.7927(3)	0.5174(4)	0.4498(3)	0.0507(9)
C21	0.5789(7)	0.3456(6)	0.3182(6)	0.078(2)
C11	0.6389(5)	0.9188(6)	0.6170(6)	0.0646(18)
C22	0.8695(6)	0.4941(6)	0.3774(6)	0.0658(19)
C12	0.7028(6)	0.0026(6)	0.3923(5)	0.0643(18)
C23	0.7482(7)	0.6049(6)	0.6507(5)	0.0693(19)
C14	0.0779(6)	0.2131(4)	0.5371(5)	0.0600(17)
C13	0.0533(7)	0.8425(5)	0.7034(5)	0.0664(18)
C24	0.3464(5)	0.6702(5)	0.4299(5)	0.0599(17)

Table S2.5. Bond lengths (Å) for Compound 2.

W1-O5	1.700(3)	W1-O3	1.869(3)
W1-O1	1.884(3)	W1-O2	1.888(4)
W1-O4	2.033(3)	W1-O4#2	2.231(3)
W2-O15	1.703(4)	W2-O11	1.872(4)
W2-O13	1.871(3)	W2-O12	1.898(4)
W2-O14	2.027(3)	W2-O14#1	2.240(3)
O4-C14	1.437(6)	O14-C24	1.432(6)
O2-C12	1.409(7)	O11-C21	1.421(7)
O1-C11	1.419(6)	O3-C13	1.409(6)
O13-C23	1.398(7)	O12-C22	1.407(7)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, -y+1, -z+1

#2 -x+2, -y+2, -z+1

Table S2.6. Bond angles (°) for Compound 2.

O5-W1-O3	97.96(18)	O5-W1-O1	105.00(18)
O3-W1-O1	85.73(16)	O5-W1-O2	95.51(18)
O3-W1-O2	166.30(16)	O1-W1-O2	88.43(17)
O5-W1-O4	94.34(16)	O3-W1-O4	90.38(14)
O1-W1-O4	160.61(14)	O2-W1-O4	91.05(15)
O5-W1-O4#2	163.18(15)	O3-W1-O4#2	83.85(14)
O1-W1-O4#2	91.80(14)	O2-W1-O4#2	83.96(14)
O4-W1-O4#2	68.88(12)	O15-W2-O11	96.12(19)
O15-W2-O13	97.93(18)	O11-W2-O13	165.87(17)
O15-W2-O12	104.75(18)	O11-W2-O12	89.45(18)
O13-W2-O12	85.58(17)	O15-W2-O14	93.73(16)
O11-W2-O14	90.73(15)	O13-W2-O14	89.81(14)
O12-W2-O14	161.39(15)	O15-W2-O14#1	162.82(15)
O11-W2-O14#1	83.92(15)	O13-W2-O14#1	83.09(14)
O12-W2-O14#1	92.43(14)	O14-W2-O14#1	69.09(13)
C14-O4-W1	122.9(3)	C14-O4-W1#2	125.9(3)
W1-O4-W1#2	111.12(12)	C24-O14-W2	123.8(3)
C24-O14-W2#1	125.3(3)	W2-O14-W2#1	110.91(13)
C12-O2-W1	135.9(4)	C21-O11-W2	139.8(5)
C11-O1-W1	131.8(4)	C13-O3-W1	137.0(4)
C23-O13-W2	136.2(4)	C22-O12-W2	131.8(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, -y+1, -z+1

#2 -x+2, -y+2, -z+1

Table S2.7. Anisotropic atomic displacement parameters (Å^2) for Compound 2.

The anisotropic atomic displacement factor exponent takes the form:
$-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.03062(10)	0.02642(10)	0.03129(12)	-0.00164(7)	0.00741(7)	-0.00020(6)
W2	0.03294(11)	0.03148(11)	0.03120(12)	0.00249(7)	0.00794(7)	-0.00418(7)
O4	0.0363(16)	0.0198(14)	0.0384(18)	-0.0024(12)	0.0094(13)	-0.0064(12)
O14	0.0323(16)	0.0277(16)	0.0381(18)	0.0079(13)	0.0074(13)	0.0036(12)
O2	0.0381(18)	0.050(2)	0.044(2)	0.0019(16)	0.0005(15)	0.0067(16)
O11	0.056(2)	0.054(2)	0.038(2)	-0.0115(17)	0.0137(17)	-0.0096(18)
O1	0.0373(19)	0.042(2)	0.066(3)	0.0038(17)	0.0184(17)	-0.0057(15)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O5	0.059(2)	0.040(2)	0.052(2)	-0.0124(17)	0.0126(18)	0.0067(17)
O3	0.0425(19)	0.0420(19)	0.037(2)	0.0078(15)	0.0028(15)	0.0015(15)
O13	0.047(2)	0.045(2)	0.041(2)	-0.0088(16)	0.0075(15)	-0.0117(16)
O15	0.056(2)	0.049(2)	0.050(2)	0.0162(18)	0.0092(18)	-0.0108(18)
O12	0.0376(19)	0.065(3)	0.052(2)	0.0024(19)	0.0145(17)	0.0029(17)
C21	0.088(5)	0.064(4)	0.087(6)	-0.035(4)	0.033(4)	-0.021(4)
C11	0.037(3)	0.071(4)	0.091(5)	-0.010(4)	0.024(3)	-0.016(3)
C22	0.050(3)	0.073(4)	0.080(5)	-0.016(4)	0.031(3)	0.000(3)
C12	0.040(3)	0.101(5)	0.047(4)	-0.008(3)	-0.007(3)	-0.004(3)
C23	0.073(4)	0.081(5)	0.047(4)	-0.003(3)	-0.009(3)	-0.017(4)
C14	0.076(4)	0.029(3)	0.080(5)	-0.017(3)	0.030(3)	-0.021(3)
C13	0.075(4)	0.048(3)	0.073(5)	0.019(3)	0.000(3)	0.005(3)
C24	0.048(3)	0.048(3)	0.085(5)	0.027(3)	0.012(3)	0.017(3)

Table S2.8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for Compound 2.

	x/a	y/b	z/c	U(eq)
H21A	0.5382	0.3313	0.2525	0.116000
H21B	0.6685	0.3235	0.3255	0.116000
H21C	0.5360	0.3020	0.3624	0.116000
H11A	0.6107	0.8473	0.6406	0.097000
H11B	0.6174	0.9799	0.6578	0.097000
H11C	0.5965	0.9312	0.5515	0.097000
H22A	0.9544	0.4705	0.4075	0.099000
H22B	0.8302	0.4341	0.3358	0.099000
H22C	0.8765	0.5619	0.3395	0.099000
H12A	0.6451	1.0539	0.3526	0.097000
H12B	0.7653	0.9729	0.3549	0.097000
H12C	0.6540	0.9405	0.4137	0.097000
H23A	0.7530	0.6678	0.6956	0.104000
H23B	0.7093	0.5402	0.6774	0.104000
H23C	0.8340	0.5851	0.6395	0.104000
H14A	1.1460	1.2297	0.5000	0.090000
H14B	1.0066	1.2643	0.5180	0.090000
H14C	1.1097	1.2229	0.6052	0.090000
H13A	1.1235	0.8446	0.7569	0.100000
H13B	0.9812	0.8023	0.7228	0.100000
H13C	1.0809	0.8038	0.6492	0.100000
H24A	0.2632	0.6580	0.4495	0.090000

	x/a	y/b	z/c	U(eq)
H24B	0.3820	0.7413	0.4563	0.090000
H24C	0.3368	0.6728	0.3601	0.090000

Crystal Structure Report for Compound 3

A specimen of $C_{22}H_{72}Li_2O_{51}W_{12}$, approximate dimensions 0.160 mm x 0.240 mm x 0.300 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å).

Table S3.1: Data collection details for Compound 3.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA
Omega	59.429	-28.00	-28.00	0.00	54.76	0.30	600	3.00	0.71076	50	20.0
Omega	59.429	-28.00	-28.00	90.00	54.76	0.30	600	3.00	0.71076	50	20.0
Omega	59.429	-28.00	-28.00	180.00	54.76	0.30	600	3.00	0.71076	50	20.0
Omega	59.429	-28.00	-28.00	270.00	54.76	0.30	600	3.00	0.71076	50	20.0

A total of 2400 frames were collected. The total exposure time was 2.00 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 35958 reflections to a maximum θ angle of 28.00° (0.76 Å resolution), of which 7916 were independent (average redundancy 4.542, completeness = 99.1%, R_{int} = 4.87%, R_{sig} = 4.16%) and 6953 (87.83%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.917(2) Å, b = 11.3231(17) Å, c = 22.002(3) Å, β = 107.241(7)°, volume = 3311.4(9) $Å^3$, are based upon the refinement of the XYZ-centroids of 9914 reflections above 20 σ(I) with 5.290° < 2θ < 68.95°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.501. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.0620 and 0.1350.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/n 1, with Z = 2 for the formula unit, $C_{22}H_{72}Li_2O_{51}W_{12}$. The final anisotropic full-matrix least-squares refinement on F^2 with 404 variables converged at R1 = 3.09%, for the observed data and wR2 = 8.39% for all data. The goodness-of-fit was 1.111. The largest peak in the final difference electron density synthesis was 1.631 $e^-/Å^3$ and the largest hole was -2.073 $e^-/Å^3$ with an RMS deviation of 0.211 $e^-/Å^3$. On the basis of the final model, the calculated density was 3.383 g/cm^3 and F(000), 3012 e^-.

Table S3.2. Sample and crystal data for Compound 3.

Identification code	WOMeNW_231117
Chemical formula	$C_{22}H_{72}Li_2O_{51}W_{12}$
Formula weight	3372.87 g/mol

Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal size	0.160 x 0.240 x 0.300 mm	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 13.917(2) Å	α = 90°
	b = 11.3231(17) Å	β = 107.241(7)°
	c = 22.002(3) Å	γ = 90°
Volume	3311.4(9) $Å^3$	
Z	2	
Density (calculated)	3.383 g/cm^3	
Absorption coefficient	20.847 mm^{-1}	
F(000)	3012	

Table S3.3. Data collection and structure refinement for Compound 3.

Theta range for data collection	2.65 to 28.00°	
Index ranges	-18<=h<=18, -14<=k<=14, -29<=l<=29	
Reflections collected	35958	
Independent reflections	7916 [R(int) = 0.0487]	
Coverage of independent reflections	99.1%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.1350 and 0.0620	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014 (Sheldrick 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	7916 / 36 / 404	
Goodness-of-fit on F^2	1.111	
Δ/σ_{max}	0.002	
Final R indices	6953 data; I>2σ(I)	R1 = 0.0309, wR2 = 0.0815
	all data	R1 = 0.0379, wR2 = 0.0839
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0387P)^2+8.3019P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.631 and -2.073 $eÅ^{-3}$	
R.M.S. deviation from mean	0.211 $eÅ^{-3}$	

Table S3.4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for Compound 3.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
W1	0.62941(2)	0.45719(2)	0.55237(2)	0.02242(7)
W2	0.47082(2)	0.50885(3)	0.66262(2)	0.02884(8)
W3	0.45246(2)	0.24382(3)	0.59470(2)	0.03079(8)
W4	0.24463(2)	0.38669(3)	0.60085(2)	0.03590(9)
W5	0.23392(2)	0.23658(3)	0.45152(2)	0.03496(8)
W6	0.26632(2)	0.70596(3)	0.57755(2)	0.04396(10)
O23	0.500000	0.500000	0.500000	0.0232(13)
O22	0.3847(3)	0.4080(4)	0.5897(2)	0.0265(10)
O21	0.3933(4)	0.6389(5)	0.6311(2)	0.0355(12)
O20	0.7309(4)	0.4011(5)	0.6271(2)	0.0337(11)
O19	0.5545(4)	0.3038(4)	0.5702(2)	0.0290(10)
O18	0.3617(4)	0.2024(5)	0.5177(2)	0.0360(12)
O17	0.2149(4)	0.5405(5)	0.5805(3)	0.0389(13)
O16	0.6875(4)	0.5952(4)	0.5532(2)	0.0299(10)
O15	0.3263(4)	0.2316(5)	0.6306(3)	0.0425(14)
C15	0.2907(17)	0.111(2)	0.6423(12)	0.075(8)
O15A	0.3263(4)	0.2316(5)	0.6306(3)	0.0425(14)
C15A	0.316(2)	0.170(3)	0.6863(14)	0.073(9)
O14	0.3405(4)	0.4476(6)	0.6869(2)	0.0426(14)
O13	0.6727(3)	0.3763(5)	0.4975(2)	0.0316(11)
O12	0.1993(4)	0.3200(5)	0.5219(2)	0.0382(12)
O11	0.5113(4)	0.3311(5)	0.6825(2)	0.0354(12)
O10	0.4962(5)	0.1094(5)	0.6292(3)	0.0515(16)
O9	0.3298(5)	0.8407(6)	0.5615(4)	0.0582(17)
O8	0.1239(4)	0.3138(6)	0.3966(3)	0.0473(15)
O7	0.5673(3)	0.5236(4)	0.6257(2)	0.0282(10)
O6	0.1492(5)	0.7222(7)	0.5095(4)	0.0616(18)
O5	0.2907(5)	0.1888(6)	0.3903(3)	0.0486(15)
O4	0.5273(4)	0.5466(6)	0.7411(2)	0.0422(14)
O3	0.1730(5)	0.1092(6)	0.4595(3)	0.0568(17)
O2	0.1557(5)	0.3456(7)	0.6374(3)	0.0592(19)
O1	0.2247(5)	0.7607(7)	0.6376(4)	0.072(2)
C6	0.0937(8)	0.6475(13)	0.4601(5)	0.075(4)
C5	0.3814(11)	0.1966(11)	0.3734(8)	0.090(5)
O1A	0.4695(6)	0.7788(7)	0.7977(4)	0.072(2)
O2A	0.6912(5)	0.6788(6)	0.8443(4)	0.078(3)
C20	0.7808(8)	0.4672(10)	0.6822(5)	0.063(3)
O3A	0.5277(6)	0.5509(9)	0.8874(4)	0.079(3)

	x/a	y/b	z/c	U(eq)
C1A	0.4536(8)	0.8522(11)	0.7452(5)	0.067(3)
C14	0.3086(9)	0.4932(11)	0.7372(6)	0.070(3)
C8	0.0224(9)	0.3247(16)	0.3942(7)	0.101(5)
C9	0.3626(13)	0.8959(11)	0.5165(8)	0.103(5)
Li1	0.5526(11)	0.6432(14)	0.8196(7)	0.048(4)
C2A	0.7547(10)	0.5944(13)	0.8403(7)	0.083(4)
C11	0.5660(12)	0.2870(14)	0.7406(8)	0.100(5)
C3A	0.4612(14)	0.5606(18)	0.9198(9)	0.128(6)

Table S3.5. Bond lengths (Å) for Compound 3.

W1-O13	1.758(5)	W1-O16	1.757(5)
W1-O23	1.8911(4)	W1-O20	1.931(5)
W1-O19	2.121(5)	W1-O7	2.178(5)
W2-O4	1.726(5)	W2-O7	1.771(5)
W2-O21	1.836(5)	W2-O22	2.043(4)
W2-O11	2.101(6)	W2-O14	2.151(5)
W3-O10	1.729(6)	W3-O19	1.795(5)
W3-O18	1.848(5)	W3-O22	2.073(5)
W3-O11	2.108(5)	W3-O15	2.132(6)
W3-O15A	2.132(6)	W4-O2	1.727(6)
W4-O17	1.815(6)	W4-O12	1.827(5)
W4-O22	2.049(4)	W4-O14	2.083(5)
W4-O15A	2.089(6)	W4-O15	2.089(6)
W5-O3	1.708(6)	W5-O5	1.833(6)
W5-O8	1.864(6)	W5-O18	1.974(5)
W5-O12	1.990(5)	W5-O16#1	2.214(5)
W6-O1	1.708(7)	W6-O9	1.848(7)
W6-O6	1.868(7)	W6-O21	1.963(5)
W6-O17	2.014(6)	W6-O13#1	2.268(5)
O20-C20	1.418(10)	O15-C15	1.50(2)
O15A-C15A	1.46(3)	O14-C14	1.408(12)
O11-C11	1.372(16)	O9-C9	1.360(15)
O8-C8	1.404(13)	O6-C6	1.413(13)
O5-C5	1.420(12)	O4-Li1	1.985(15)
O1A-C1A	1.387(13)	O1A-Li1	1.896(18)
O2A-C2A	1.322(14)	O2A-Li1	1.887(17)
O3A-C3A	1.329(18)	O3A-Li1	1.936(19)
Li1-C2A	2.77(2)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1, -y+1, -z+1

Table S3.6. Bond angles (°) for Compound 3.

O13-W1-O16	102.7(2)	O13-W1-O23	99.97(16)
O16-W1-O23	97.48(16)	O13-W1-O20	95.8(2)
O16-W1-O20	93.8(2)	O23-W1-O20	158.07(16)
O13-W1-O19	89.3(2)	O16-W1-O19	167.5(2)
O23-W1-O19	83.76(14)	O20-W1-O19	81.3(2)
O13-W1-O7	168.7(2)	O16-W1-O7	88.2(2)
O23-W1-O7	81.22(13)	O20-W1-O7	80.4(2)
O19-W1-O7	79.67(18)	O4-W2-O7	104.6(2)
O4-W2-O21	102.8(3)	O7-W2-O21	101.1(2)
O4-W2-O22	155.7(2)	O7-W2-O22	92.3(2)
O21-W2-O22	90.6(2)	O4-W2-O11	90.8(3)
O7-W2-O11	89.6(2)	O21-W2-O11	159.8(2)
O22-W2-O11	71.7(2)	O4-W2-O14	90.0(2)
O7-W2-O14	162.4(2)	O21-W2-O14	84.7(2)
O22-W2-O14	70.88(19)	O11-W2-O14	80.4(2)
O10-W3-O19	104.9(3)	O10-W3-O18	103.6(3)
O19-W3-O18	102.0(2)	O10-W3-O22	155.2(3)
O19-W3-O22	91.9(2)	O18-W3-O22	90.1(2)
O10-W3-O11	91.1(3)	O19-W3-O11	88.3(2)
O18-W3-O11	158.9(2)	O22-W3-O11	71.03(19)
O10-W3-O15	90.1(3)	O19-W3-O15	161.3(2)
O18-W3-O15	84.8(2)	O22-W3-O15	70.5(2)
O11-W3-O15	80.2(2)	O10-W3-O15A	90.1(3)
O19-W3-O15A	161.3(2)	O18-W3-O15A	84.8(2)
O22-W3-O15A	70.5(2)	O11-W3-O15A	80.2(2)
O2-W4-O17	103.3(3)	O2-W4-O12	103.8(3)
O17-W4-O12	100.0(3)	O2-W4-O22	157.7(3)
O17-W4-O22	90.7(2)	O12-W4-O22	90.4(2)
O2-W4-O14	91.2(3)	O17-W4-O14	86.8(3)
O12-W4-O14	161.5(2)	O22-W4-O14	72.16(19)
O2-W4-O15A	91.5(3)	O17-W4-O15A	161.2(2)
O12-W4-O15A	87.3(2)	O22-W4-O15A	71.8(2)
O14-W4-O15A	81.4(2)	O2-W4-O15	91.5(3)
O17-W4-O15	161.2(2)	O12-W4-O15	87.3(2)
O22-W4-O15	71.8(2)	O14-W4-O15	81.4(2)
O3-W5-O5	99.3(3)	O3-W5-O8	97.2(3)
O5-W5-O8	96.4(3)	O3-W5-O18	97.2(3)
O5-W5-O18	89.7(3)	O8-W5-O18	163.3(2)
O3-W5-O12	94.5(3)	O5-W5-O12	165.4(2)
O8-W5-O12	86.6(2)	O18-W5-O12	83.8(2)
O3-W5-O16#1	176.6(3)	O5-W5-O16#1	83.9(2)

O8-W5-O16#1	83.6(2)	O18-W5-O16#1	81.59(19)
O12-W5-O16#1	82.2(2)	O1-W6-O9	98.0(4)
O1-W6-O6	99.7(3)	O9-W6-O6	96.8(3)
O1-W6-O21	97.3(3)	O9-W6-O21	92.2(3)
O6-W6-O21	159.4(3)	O1-W6-O17	96.2(3)
O9-W6-O17	165.6(3)	O6-W6-O17	83.3(3)
O21-W6-O17	83.5(2)	O1-W6-O13#1	176.1(3)
O9-W6-O13#1	84.1(3)	O6-W6-O13#1	83.3(3)
O21-W6-O13#1	79.27(19)	O17-W6-O13#1	81.7(2)
W1-O23-W1#1	180.000000	W2-O22-W4	109.2(2)
W2-O22-W3	107.9(2)	W4-O22-W3	108.8(2)
W2-O21-W6	149.4(3)	C20-O20-W1	127.1(6)
W3-O19-W1	147.2(3)	W3-O18-W5	148.0(3)
W4-O17-W6	147.5(3)	W1-O16-W5#1	175.4(3)
C15-O15-W4	130.0(9)	C15-O15-W3	118.2(10)
W4-O15-W3	105.1(2)	C15A-O15A-W4	119.3(12)
C15A-O15A-W3	129.7(12)	W4-O15A-W3	105.1(2)
C14-O14-W4	124.7(6)	C14-O14-W2	124.2(6)
W4-O14-W2	104.0(2)	W1-O13-W6#1	172.8(3)
W4-O12-W5	147.2(3)	C11-O11-W2	125.7(8)
C11-O11-W3	129.8(8)	W2-O11-W3	104.5(2)
C9-O9-W6	143.2(8)	C8-O8-W5	133.6(8)
W2-O7-W1	146.0(3)	C6-O6-W6	134.9(7)
C5-O5-W5	141.6(7)	W2-O4-Li1	156.5(6)
C1A-O1A-Li1	129.2(8)	C2A-O2A-Li1	118.2(9)
C3A-O3A-Li1	132.8(12)	O2A-Li1-O1A	113.2(9)
O2A-Li1-O3A	107.1(8)	O1A-Li1-O3A	113.5(9)
O2A-Li1-O4	105.7(8)	O1A-Li1-O4	106.8(7)
O3A-Li1-O4	110.3(8)	O2A-Li1-C2A	24.9(4)
O1A-Li1-C2A	135.8(9)	O3A-Li1-C2A	99.8(7)
O4-Li1-C2A	86.7(7)	O2A-C2A-Li1	36.9(6)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1, -y+1, -z+1

Table S3.7. Anisotropic atomic displacement parameters (Å^2) for Compound 3.

The anisotropic atomic displacement factor exponent takes the form:
$-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01774(12)	0.02689(14)	0.02121(13)	0.00119(10)	0.00358(10)	-0.00224(9)
W2	0.02357(14)	0.04277(18)	0.02022(13)	-0.00699(11)	0.00653(10)	-0.00864(11)
W3	0.03068(15)	0.02972(16)	0.02994(15)	0.00530(11)	0.00583(12)	-0.00848(11)
W4	0.02550(14)	0.0580(2)	0.02655(15)	-0.00716(13)	0.01138(11)	-0.01606(13)
W5	0.03128(16)	0.04069(18)	0.03111(16)	-0.00951(12)	0.00647(12)	-0.01489(12)
W6	0.02828(16)	0.0508(2)	0.0506(2)	-0.01563(16)	0.00823(14)	0.00461(14)
O23	0.025(3)	0.025(3)	0.018(3)	0.002(2)	0.005(3)	-0.004(2)
O22	0.025(2)	0.034(3)	0.021(2)	-0.0034(19)	0.0068(18)	-0.0117(19)
O21	0.026(2)	0.041(3)	0.038(3)	-0.014(2)	0.006(2)	-0.003(2)
O20	0.029(3)	0.039(3)	0.026(2)	0.003(2)	-0.001(2)	0.001(2)
O19	0.029(2)	0.029(3)	0.031(3)	-0.002(2)	0.011(2)	-0.0088(19)
O18	0.038(3)	0.033(3)	0.033(3)	0.000(2)	0.004(2)	-0.012(2)
O17	0.025(3)	0.058(4)	0.036(3)	-0.007(3)	0.012(2)	-0.006(2)
O16	0.027(2)	0.036(3)	0.025(2)	0.003(2)	0.0061(19)	-0.009(2)
O15	0.042(3)	0.050(3)	0.033(3)	0.010(2)	0.008(2)	-0.022(3)
C15	0.075(8)	0.074(8)	0.075(8)	0.001(2)	0.023(3)	-0.001(2)
O15A	0.042(3)	0.050(3)	0.033(3)	0.010(2)	0.008(2)	-0.022(3)
C15A	0.073(9)	0.074(9)	0.073(9)	0.001(2)	0.021(3)	-0.001(2)
O14	0.034(3)	0.072(4)	0.024(3)	-0.010(3)	0.011(2)	-0.015(3)
O13	0.024(2)	0.039(3)	0.030(3)	-0.005(2)	0.006(2)	0.001(2)
O12	0.025(2)	0.056(4)	0.033(3)	-0.006(2)	0.007(2)	-0.012(2)
O11	0.034(3)	0.044(3)	0.024(2)	0.008(2)	0.003(2)	-0.006(2)
O10	0.046(3)	0.041(3)	0.060(4)	0.018(3)	0.004(3)	-0.009(3)
O9	0.054(4)	0.043(4)	0.074(5)	-0.011(3)	0.013(3)	0.004(3)
O8	0.031(3)	0.072(4)	0.035(3)	-0.005(3)	0.005(2)	-0.004(3)
O7	0.024(2)	0.038(3)	0.023(2)	-0.004(2)	0.0078(19)	-0.0049(19)
O6	0.035(3)	0.073(5)	0.071(5)	-0.004(4)	0.006(3)	0.012(3)
O5	0.055(4)	0.052(4)	0.040(3)	-0.016(3)	0.016(3)	-0.008(3)
O4	0.040(3)	0.061(4)	0.024(3)	-0.013(2)	0.008(2)	-0.017(3)
O3	0.056(4)	0.056(4)	0.059(4)	-0.007(3)	0.017(3)	-0.028(3)
O2	0.048(4)	0.090(5)	0.049(4)	-0.011(3)	0.029(3)	-0.031(3)
O1	0.045(4)	0.089(6)	0.086(5)	-0.044(4)	0.022(4)	0.009(4)
C6	0.052(6)	0.118(11)	0.043(6)	0.007(6)	-0.004(5)	-0.012(6)
C5	0.096(10)	0.067(8)	0.141(13)	-0.017(8)	0.088(10)	-0.016(7)
O1A	0.074(5)	0.093(6)	0.061(5)	0.014(4)	0.039(4)	0.041(4)
O2A	0.037(3)	0.051(4)	0.127(7)	-0.031(4)	-0.005(4)	-0.003(3)
C20	0.056(6)	0.073(7)	0.041(5)	-0.003(5)	-0.018(4)	-0.003(5)
O3A	0.071(5)	0.108(7)	0.058(5)	0.030(5)	0.020(4)	0.031(5)
C1A	0.065(7)	0.081(8)	0.050(6)	-0.009(5)	0.010(5)	0.005(6)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C14	0.069(3)	0.074(4)	0.068(3)	-0.0035(19)	0.024(2)	-0.0030(19)
C8	0.046(7)	0.161(16)	0.092(10)	-0.017(10)	0.011(6)	-0.011(8)
C9	0.157(15)	0.049(7)	0.122(13)	-0.014(8)	0.072(12)	-0.017(8)
Li1	0.048(8)	0.051(9)	0.034(7)	-0.015(6)	-0.002(6)	-0.004(7)
C2A	0.083(4)	0.083(4)	0.084(4)	-0.0005(10)	0.0243(14)	0.0002(10)
C11	0.101(5)	0.099(5)	0.097(5)	0.000(2)	0.026(2)	0.001(2)
C3A	0.128(6)	0.128(6)	0.128(6)	0.001(2)	0.038(3)	0.002(2)

Table S3.8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for Compound 3.

	x/a	y/b	z/c	U(eq)
H15A	0.3473	0.0584	0.6557	0.112000
H15B	0.2578	0.1154	0.6749	0.112000
H15C	0.2443	0.0815	0.6038	0.112000
H15D	0.3581	0.1005	0.6939	0.110000
H15E	0.3364	0.2207	0.7227	0.110000
H15F	0.2473	0.1465	0.6791	0.110000
H6A	0.0364	0.6894	0.4338	0.113000
H6B	0.1356	0.6230	0.4347	0.113000
H6C	0.0715	0.5794	0.4781	0.113000
H5A	0.3740	0.1541	0.3346	0.135000
H5B	0.3958	0.2780	0.3676	0.135000
H5C	0.4355	0.1631	0.4067	0.135000
H1A	0.4345	0.7989	0.8263	0.086000
H2A	0.7143	0.7538	0.8588	0.093000
H20A	0.8276	0.4172	0.7120	0.095000
H20B	0.8163	0.5318	0.6705	0.095000
H20C	0.7322	0.4973	0.7014	0.095000
H3A	0.5710	0.4869	0.8999	0.095000
H1A1	0.4072	0.9136	0.7475	0.100000
H1A2	0.5163	0.8868	0.7446	0.100000
H1A3	0.4261	0.8071	0.7070	0.100000
H14A	0.3663	0.5155	0.7717	0.105000
H14B	0.2669	0.5612	0.7227	0.105000
H14C	0.2709	0.4341	0.7515	0.105000
H8A	-0.0122	0.3723	0.3583	0.152000
H8B	-0.0079	0.2479	0.3902	0.152000
H8C	0.0179	0.3616	0.4326	0.152000
H9A	0.3930	0.9699	0.5329	0.154000
H9B	0.4113	0.8470	0.5055	0.154000
H9C	0.3067	0.9097	0.4793	0.154000
H2A1	0.8222	0.6243	0.8543	0.125000

	x/a	y/b	z/c	U(eq)
H2A2	0.7485	0.5292	0.8668	0.125000
H2A3	0.7395	0.5682	0.7970	0.125000
H11A	0.5744	0.2033	0.7372	0.149000
H11B	0.6309	0.3243	0.7537	0.149000
H11C	0.5311	0.3025	0.7714	0.149000
H3A1	0.4714	0.4979	0.9504	0.192000
H3A2	0.4698	0.6353	0.9414	0.192000
H3A3	0.3944	0.5556	0.8909	0.192000

Diffusion Analysis

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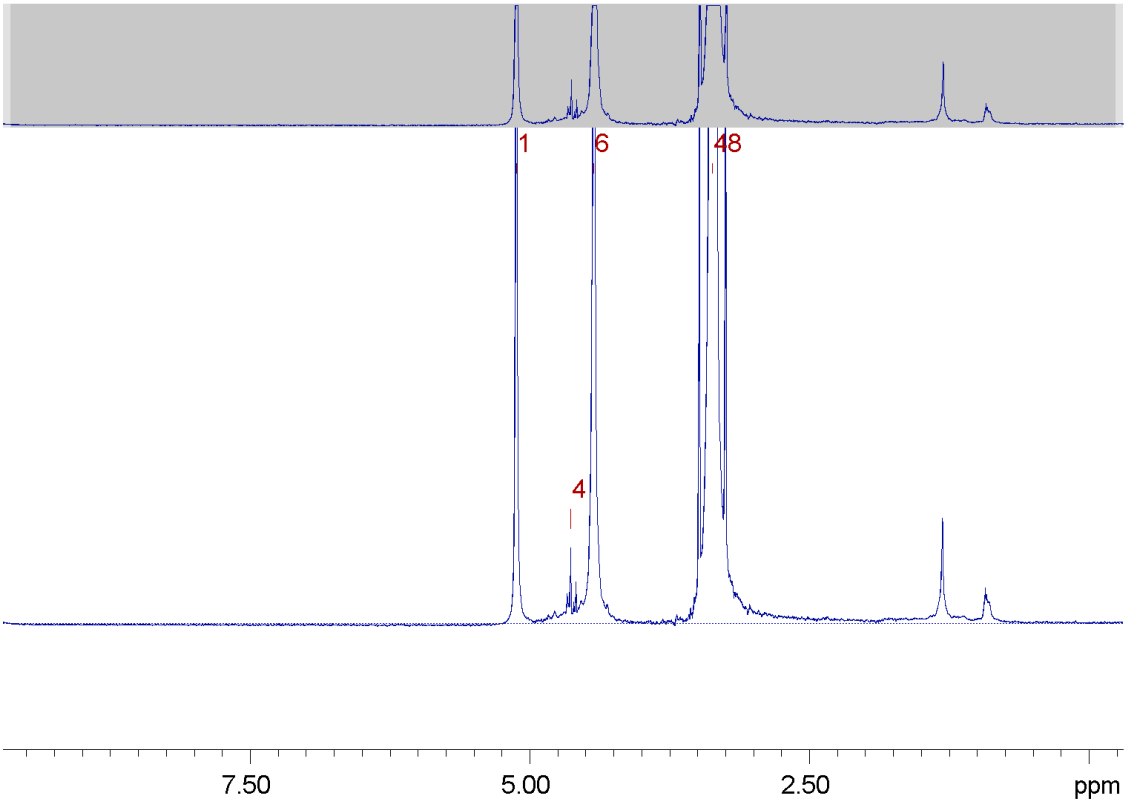
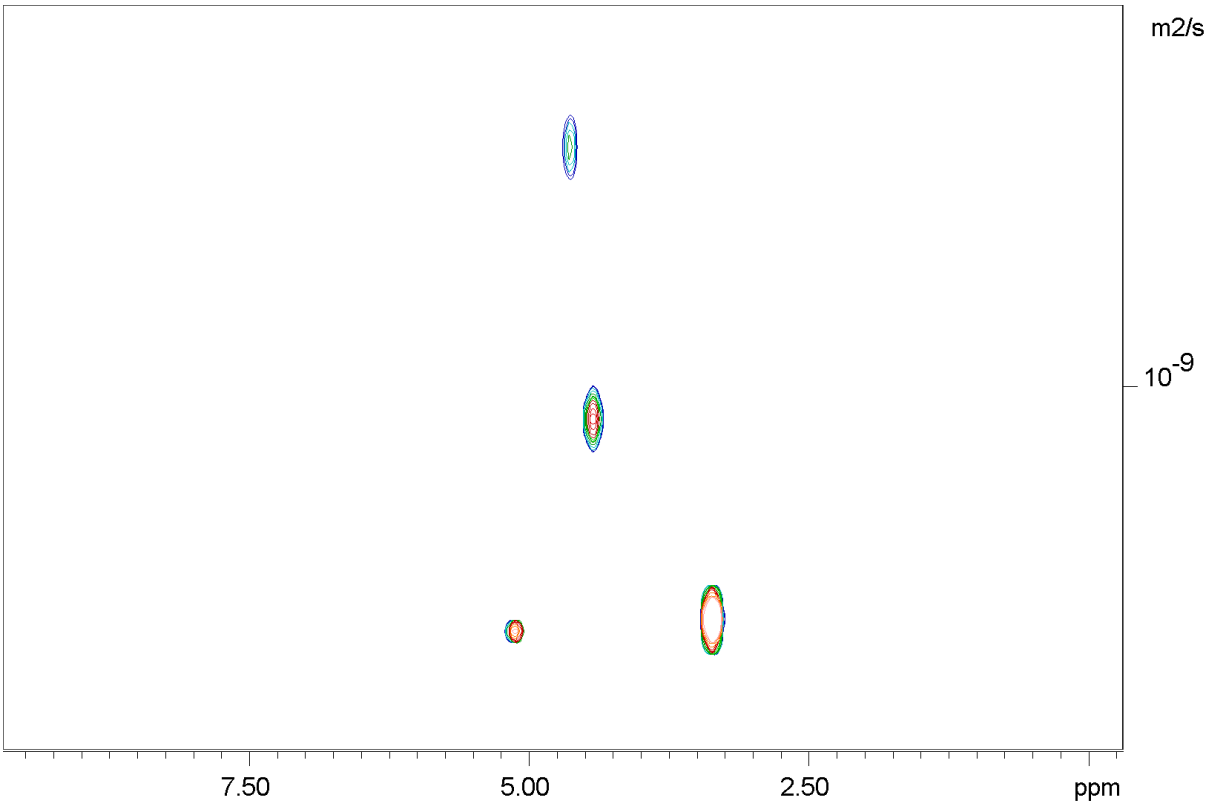
Description/Title:	
Origin:	in-house
Date of preparation:	25 Mar 2025
Lab Book Number:	000
Temperature (K):	273.0

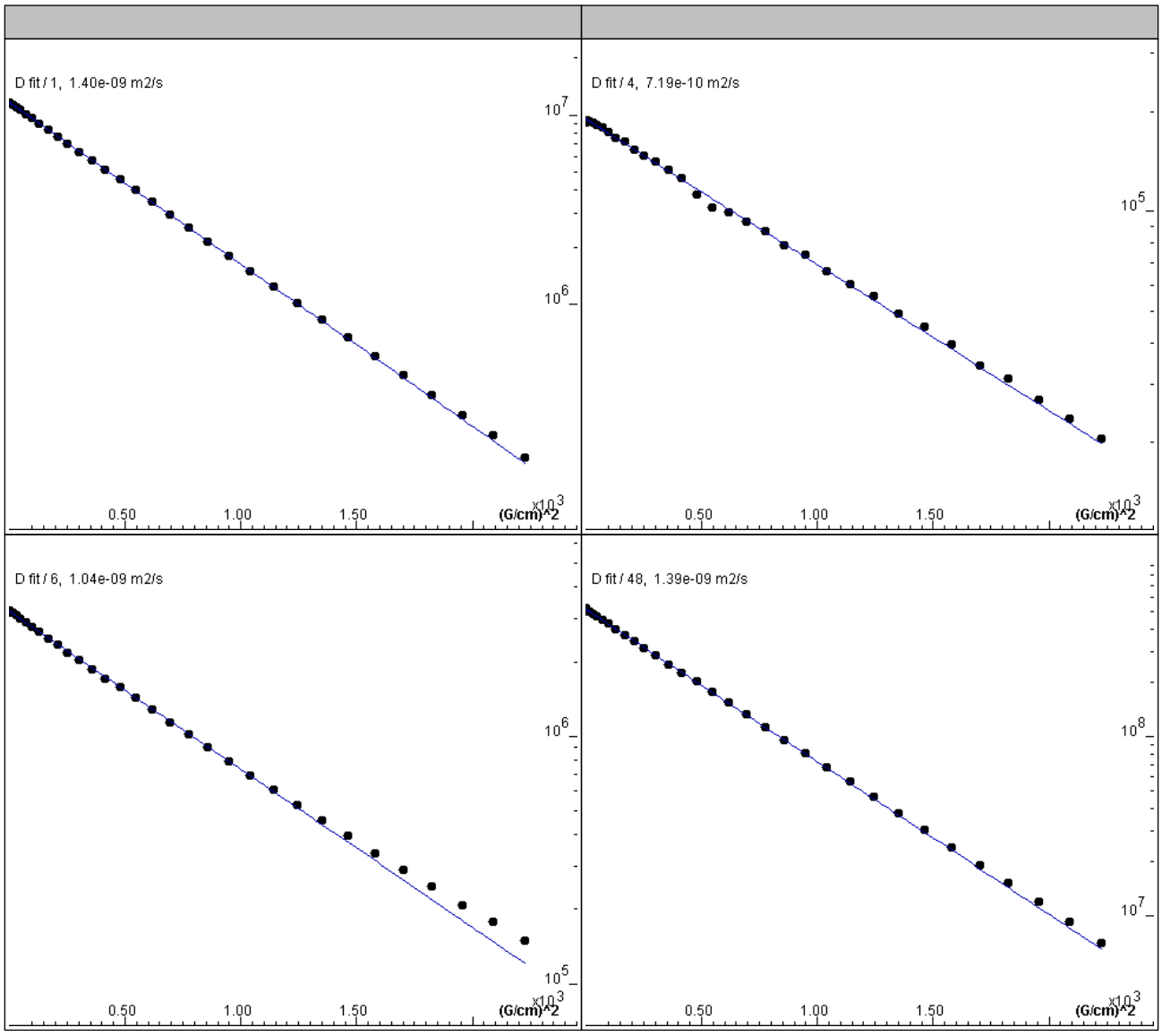


Dosy/Fit


m2/s
10-9
7.50
5.00
2.50
ppm

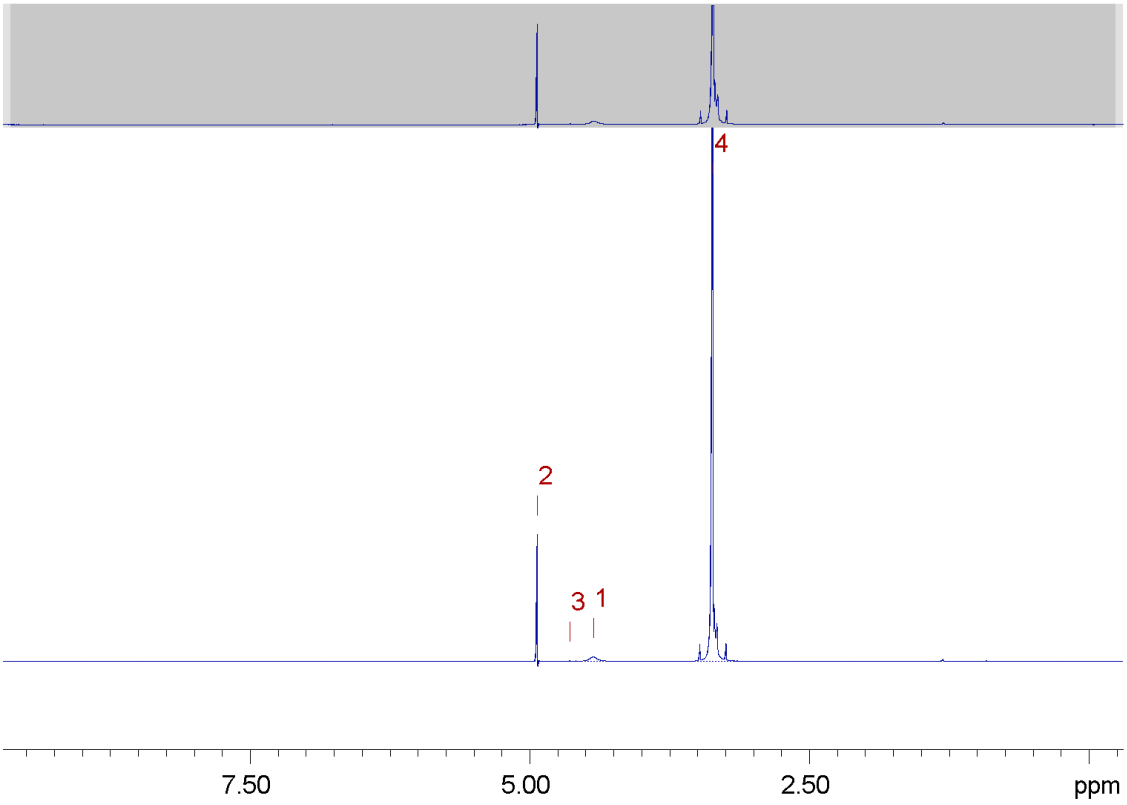
Fitted function:	f (x) = Io * exp (-D * x^2 * gamma^2 * littleDelta^2 (bigDelta-littleDelta/3)* 10^4
used gamma:	26752 rad/(s*Gauss)
used little delta:	0.0020000 s
used big delta:	0.049900 s
used gradient strength:	variable
Random error estimation of data:	RMS per spectrum (or trace/plane)
Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation method:	from fit using arbitrary y uncertainties
Confidence level:	95%
Used peaks:	
Used integrals:	peak intensities
Used Gradient strength:	all values (including replicates) used

Peak name	F2 [ppm]	D [m2/s]	error	fitInfo
1	5.118	1.40e-09	4.770e-12	Done
4	4.633	7.19e-10	1.336e-11	Done
6	4.426	1.04e-09	1.125e-11	Done
48	3.368	1.39e-09	1.219e-11	Done

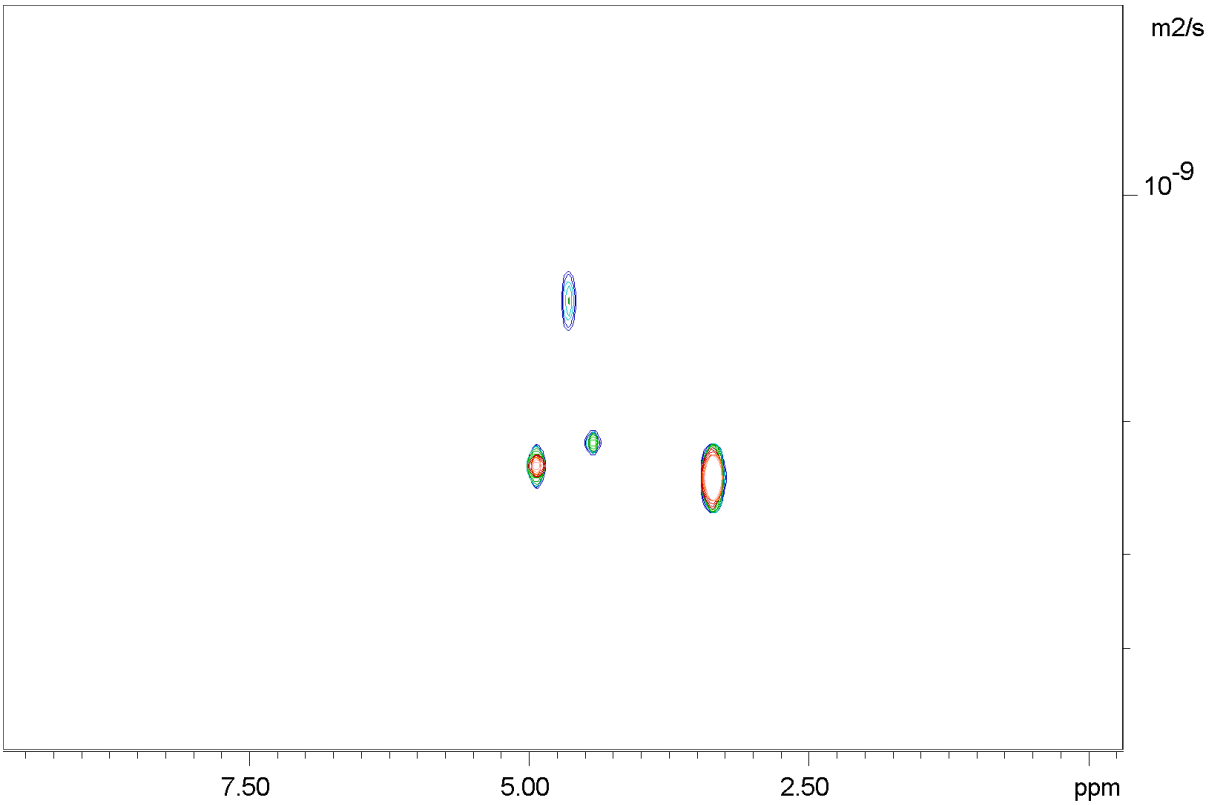

D fit / 1, 1.40e-09 m2/s
D fit / 4, 7.19e-10 m2/s
D fit / 6, 1.04e-09 m2/s
D fit / 48, 1.39e-09 m2/s
0.50
1.00
1.50
x10^3
(G/cm)^2

• Diffusion Analysis

sample name:	w293K
Description/Title:	
Origin:	in-house
Date of preparation:	25 Mar 2025
Lab Book Number:	000
Temperature (K):	293.0



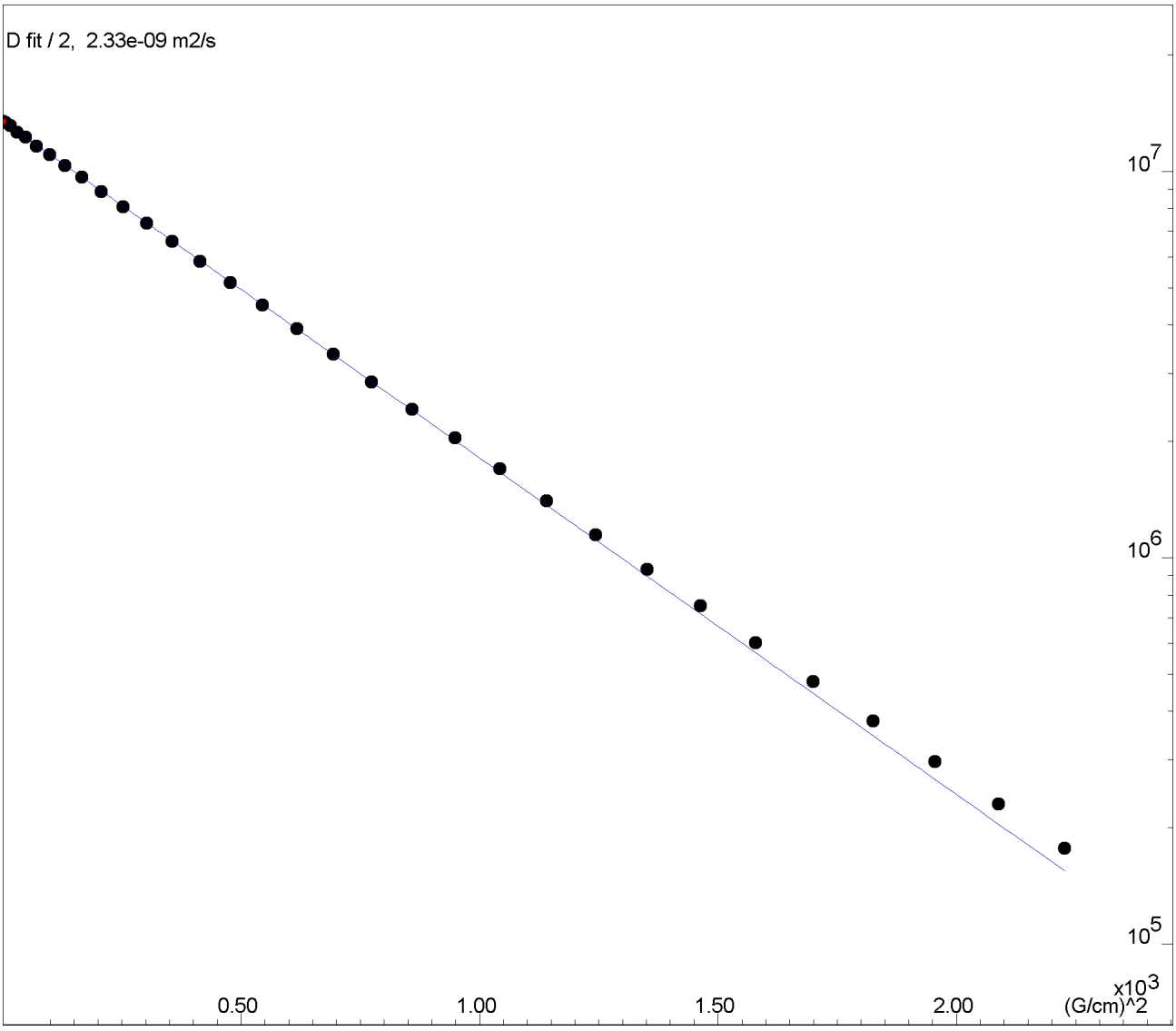
Dosy/Fit

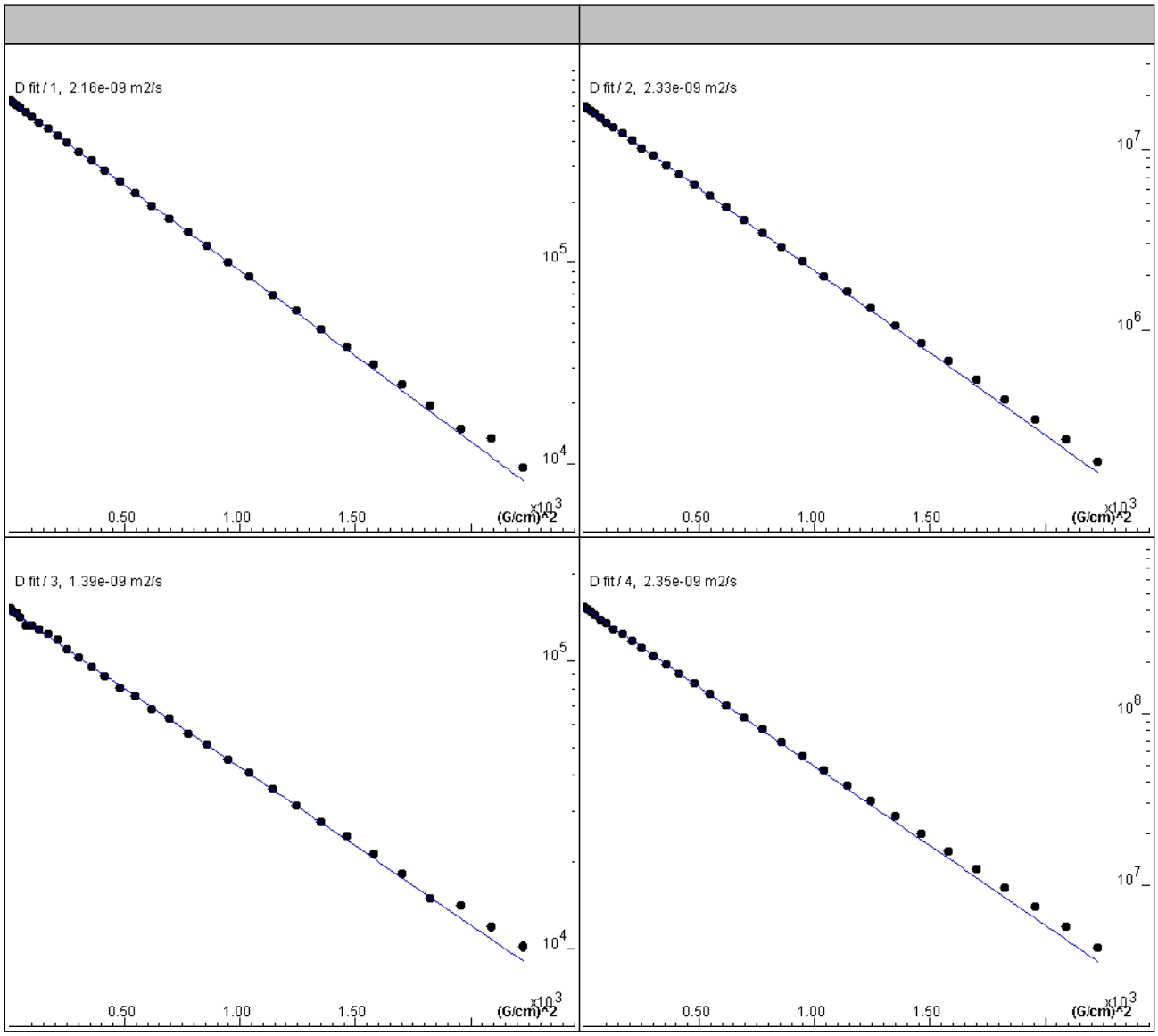

m2/s
10-9
7.50
5.00
2.50
ppm

Fitted function:	f (x) = Io * exp (-D * x^2 * gamma^2 * littleDelta^2 (bigDelta-littleDelta/3)* 10^4
used gamma:	26752 rad/(s*Gauss)
used little delta:	0.0016000 s
used big delta:	0.049900 s
used gradient strength:	variable
Random error estimation of data:	RMS per spectrum (or trace/plane)
Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation method:	from fit using arbitrary y uncertainties
Confidence level:	95%
Used peaks:	peaks from peaklist.xml at spectrum
Used integrals:	peak intensities
Used Gradient strength:	all values (including replicates) used

Peak name	F2 [ppm]	D [m2/s]	error	fitInfo
1	4.429	2.16e-09	1.107e-11	Done
2	4.932	2.33e-09	1.050e-11	Done
3	4.642	1.39e-09	2.518e-11	Done
4	3.362	2.35e-09	1.833e-11	Done

Current fit display

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D fit / 2, 2.33e-09 m2/s
D fit / 3, 1.39e-09 m2/s
D fit / 4, 2.35e-09 m2/s
0.50
1.00
1.50
x10^3
(G/cm)^2