Supporting Information for

NMR Crystallography for Structural Characterization of Oxovanadium(V) Complexes: Deriving Coordination Geometry and Detecting Weakly Coordinated Ligands at Atomic Resolution in the Solid State

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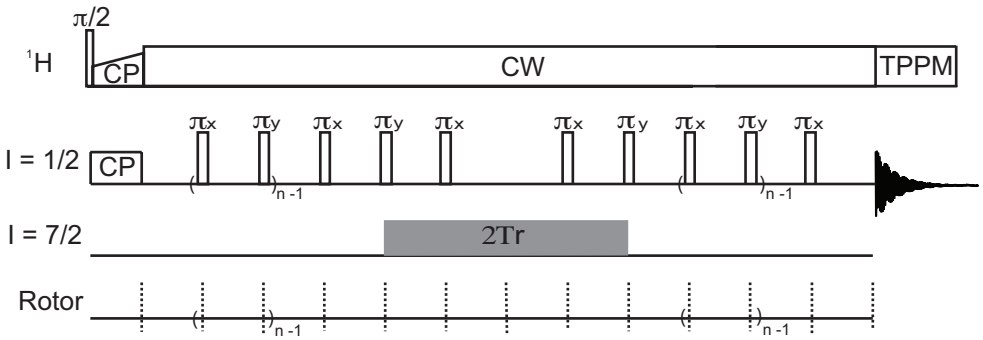

Figure S1. Low-alpha rotational echo adiabatic passage double resonance (LA-REDOR) pulse sequence.

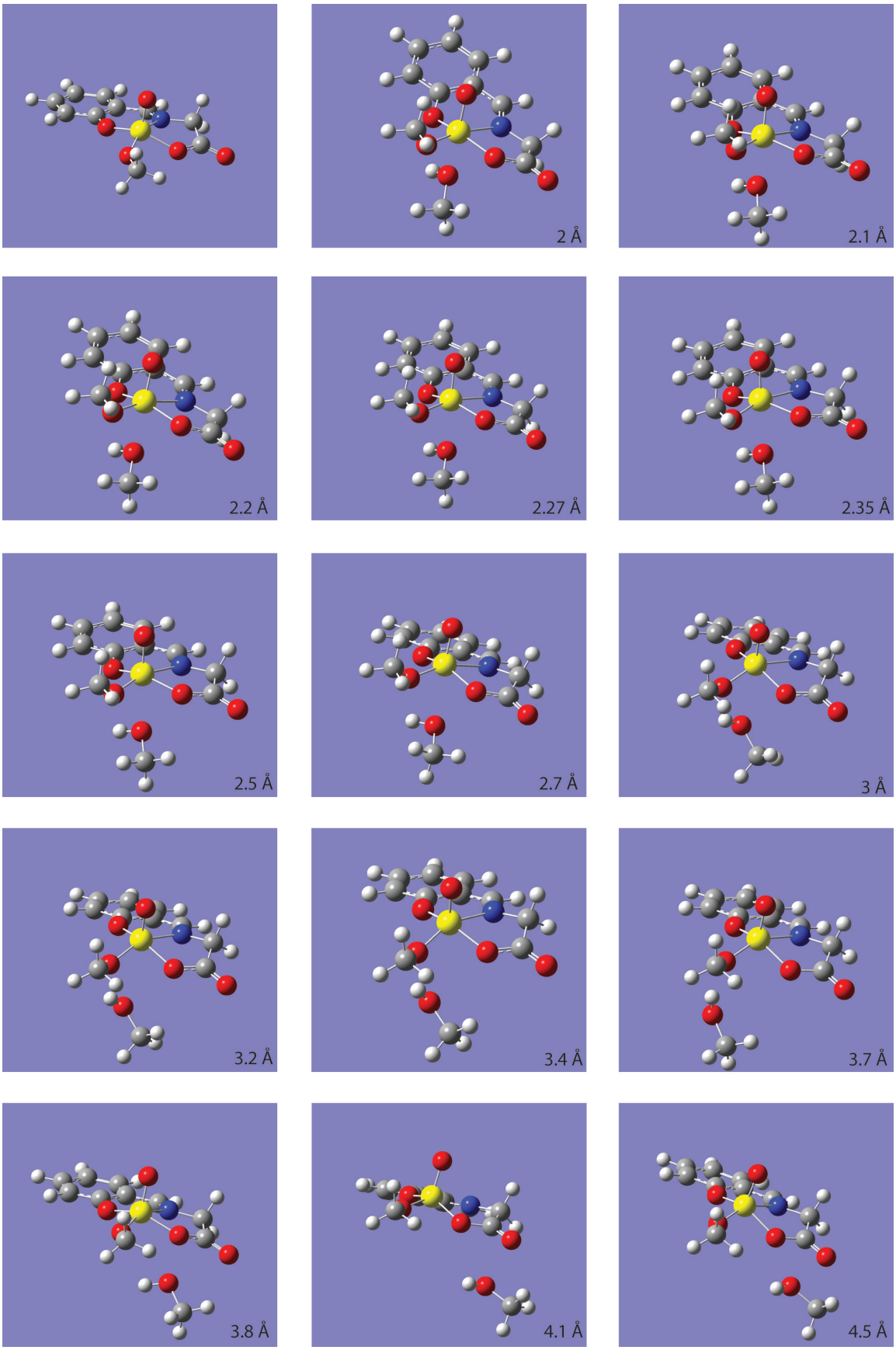

Figure S2. Structures of [$VO^{15}NGlySal(OCH_3)$] and [$VO^{15}NGlySal(OCH_3)(CH_3OH)$] with V---$OHCH_3$ of different distances. Distances are marked in each structure. These structures are optimized with Gaussian09 at B3LYP/TZV theory level and are used for NMR parameters calculations.

Table S1. Experimental and Computed ^{51}V NMR Parameters for $[VO^{15}NGlySal(OCH_3)]\cdot(CH_3OH)$ as a Function of V---$OHCH_3$ Distance.

BLYP/TZV								
V-CH_3OH (Å)	**C_Q/MHz**	**η_Q**	**δ_{iso}/ppm**	**δ_σ/ppm**	**η_σ**	**α/degree**	**β/degree**	**γ/degree**
Experiment	**3.5±0.1**	**0.73±0.05**	**-528.9±5**	**-421.4±5**	**0.31±0.05**	**0±30**	**90±30**	**90±30**
none	-4.8	0.84	-711.9	-442.5	0.23	-54.8	115	58.7
2	9.8	0.34	-591.8	-328.0	0.28	-16.1	137	13
2.1	6.8	0.44	-605.0	-328.8	0.27	-20.9	136	17.4
2.2	4.5	0.59	-617.2	-331.2	0.28	-25	133	22.1
2.27	3.3	0.77	-625.1	-333.8	0.28	-27.4	129	25.5
2.35	-2.3	0.91	-633.7	-337.5	0.28	-29.3	121	30
2.5	-1.6	0.75	-647.6	-347.5	0.27	-27.2	93.1	40.4
2.7	2.0	0.32	-659.4	-369.7	0.24	27.1	24.9	-58.6
3	3.0	0.61	-653.6	-425.8	0.18	72.4	40.1	88.6
3.2	3.0	0.65	-658.9	-435.8	0.17	77	36.6	80.5
3.4	3.0	0.66	-660.7	-434.9	0.18	83.9	30.1	72.2
3.7	3.1	0.79	-659.0	-432.2	0.19	89.7	29.4	71.3
3.8	4.1	0.80	-694.4	-431.4	0.27	-6.9	87.8	30.6
4.1	-4.1	0.99	-698.6	-436.0	0.25	-3.5	103	27
4.5	-4.6	0.77	-702.3	-441.9	0.19	15.5	123	14.6
BLYP/6-311+G								
V-CH_3OH (Å)	**C_Q/MHz**	**η_Q**	**δ_{iso}/ppm**	**δ_σ/ppm**	**η_σ**	**α/degree**	**β/degree**	**γ/degree**
Experiment	**3.5±0.1**	**0.73±0.05**	**-528.9±5**	**-421.4±5**	**0.31±0.05**	**0±30**	**90±30**	**90±30**
none	-5.6	0.78	-692.5	-432.1	0.27	-56.3	119	59.4
2	11.1	0.34	-572.4	-320.6	0.26	-15.6	137	13.4
2.1	7.8	0.44	-586.4	-320.1	0.26	-20.2	135	17.8
2.2	5.3	0.58	-598.9	-322.0	0.26	-24.2	132	22.3
2.27	3.9	0.73	-607.1	-324.4	0.27	-26.6	129	25.4
2.35	-2.7	1.00	-615.9	-328.3	0.27	-28.8	123	29.1
2.5	-1.9	0.65	-629.9	-339.2	0.26	-28	106	36.1
2.7	2.0	0.62	-640.2	-364.2	0.23	23.7	45.9	-51
3	3.2	0.81	-632.0	-421.7	0.17	77	52.9	83.3
3.2	3.2	0.86	-638.0	-430.1	0.17	81.6	50.7	77.3
3.4	3.2	0.88	-639.3	-428.5	0.19	87.7	43.8	72.1
3.7	-3.3	0.98	-639.1	-425.7	0.19	-87.9	39.8	72.3
3.8	4.6	0.89	-673.0	-422.7	0.32	-11.3	90.9	32.7
4.1	-4.8	0.90	-676.5	-426.8	0.30	-8	106	29.2
4.5	-5.4	0.67	-680.6	-431.7	0.23	11	127	18.3
B3LYP/TZV								
V-CH_3OH (Å)	**C_Q/MHz**	**η_Q**	**δ_{iso}/ppm**	**δ_σ/ppm**	**η_σ**	**α/degree**	**β/degree**	**γ/degree**
Experiment	**3.5±0.1**	**0.73±0.05**	**-528.9±5**	**-421.4±5**	**0.31±0.05**	**0±30**	**90±30**	**90±30**
none	-4.7	0.90	-947.4	-642.4	0.06	-54.7	110	59.6
2	9.9	0.33	-819.6	-480.0	0.21	-16.3	134	11.9
2.1	6.8	0.42	-832.0	-483.8	0.21	-21.2	133	16.1
2.2	4.4	0.57	-843.9	-489.1	0.21	-25.3	130	20.9
2.27	3.1	0.75	-851.7	-493.4	0.21	-27.5	125	24.8
2.35	-2.1	0.92	-860.2	-498.9	0.21	-29.1	116	30.9
2.5	-1.4	0.99	-874.3	-512.1	0.21	-25.6	73.8	47.2
2.7	2.1	0.10	-887.5	-541.4	0.20	33	15.4	-85.8
3	3.1	0.58	-883.2	-614.2	0.19	73.7	34.6	-87.3
3.2	3.1	0.60	-889.4	-624.5	0.18	77.8	29.3	83.1
3.4	3.1	0.60	-892.0	-622.6	0.17	83.9	20.8	72.6
3.7	3.1	0.73	-890.7	-620.2	0.16	89	19.5	70.6
3.8	4.2	0.71	-928.7	-626.4	0.11	-1.87	83.5	32.8
4.1	4.2	0.92	-933.4	-631.8	0.09	2.5	99.8	28.1
4.5	-4.5	0.84	-936.2	-635.6	0.06	22.7	122	13.9

Table S1 (continued). Experimental and Computed ^{51}V NMR Parameters for $[VO^{15}NGlySal(OCH_3)]\cdot(CH_3OH)$ as a Function of V---$OHCH_3$ Distance.

B3LYP/6-311+G								
V-CH_3OH (Å)	**C_Q/MHz**	**η_Q**	**δ_{iso}/ppm**	**δ_σ/ppm**	**η_σ**	**α/degree**	**β/degree**	**γ/degree**
Experiment	**3.5±0.1**	**0.73±0.05**	**-528.9±5**	**-421.4±5**	**0.31±0.05**	**0±30**	**90±30**	**90±30**
none	-5.5	0.81	-902.1	-622.8	0.09	-56.2	115	59.3
2	11.3	0.32	-776.4	-465.2	0.20	-15.7	133	12.2
2.1	7.8	0.41	-789.6	-467.1	0.20	-20.3	132	16.4
2.2	5.2	0.55	-801.7	-471.4	0.20	-24.3	130	20.9
2.27	3.8	0.70	-809.7	-475.3	0.20	-26.5	126	24.4
2.35	2.6	0.97	-818.2	-480.9	0.20	-28.3	119	29
2.5	-1.8	0.79	-832.2	-494.8	0.20	-25	133	22.1
2.7	2.1	0.40	-843.7	-526.6	0.19	30	29.1	-78.6
3	3.3	0.74	-836.5	-600.5	0.18	78.7	45.4	87.3
3.2	3.3	0.79	-843.2	-609.5	0.17	82.8	42.2	79.4
3.4	3.3	0.82	-845.2	-607.0	0.16	88.3	34.7	72
3.7	3.3	0.97	-845.1	-604.2	0.14	-87.9	31.4	71.4
3.8	4.6	0.81	-881.9	-608.1	0.14	-7.02	87.2	35.2
4.1	-4.7	0.97	-885.7	-613.2	0.13	-2.76	103	30.7
4.5	-5.3	0.72	-888.9	-616.7	0.08	18.2	126	18.2

Table S2. Experimental and Computed ^{15}N NMR Parameters for $[VO^{15}NGlySal(OCH_3)]\cdot(CH_3OH)$ as a Function of V---$OHCH_3$ Distance.

BLYP/TZV			
V-CH_3OH (Å)	**δ_{iso}/ppm**	**δ_σ/ppm (±5)**	**η_σ (±0.05)**
Experiment	**253.2**	**-209.9**	**0.73**
none	274.3	-229.0	0.82
2	280.3	-244.4	0.83
2.1	279.3	-243.4	0.82
2.2	278.5	-241.9	0.82
2.27	278.2	-240.9	0.82
2.35	278.0	-239.8	0.82
2.5	277.9	-237.8	0.84
2.7	275.4	-232.9	0.85
3	265.5	-220.0	0.84
3.2	265.4	-220.0	0.84
3.4	266.4	-220.3	0.84
3.7	267.7	-221.5	0.84
3.8	279.3	-238.5	0.77
4.1	279.1	-236.5	0.78
4.5	275.2	-228.8	0.82
BLYP/6-311+G			
V-CH_3OH (Å)	**δ_{iso}/ppm**	**δ_σ/ppm (±5)**	**η_σ (±0.05)**
Experiment	**253.2**	**-209.9**	**0.73**
none	275.1	-228.9	0.85
2	280.2	-242.6	0.85
2.1	280.2	-242.6	0.85
2.2	278.7	-240.0	0.82
2.27	278.4	-239.0	0.84
2.35	278.3	-237.8	0.85
2.5	278.0	-236.4	0.86
2.7	275.6	-231.6	0.87
3	265.5	-218.9	0.86
3.2	265.6	-219.3	0.86
3.4	266.8	-219.8	0.86
3.7	268.1	-221.1	0.86
3.8	279.6	-237.4	0.79
4.1	279.4	-236.7	0.80
4.5	275.1	-227.9	0.83
B3LYP/TZV			
V-CH_3OH (Å)	**δ_{iso}/ppm**	**δ_σ/ppm (±5)**	**η_σ (±0.05)**
Experiment	**253.2**	**-209.9**	**0.73**
none	282.1	-238.3	0.80
2	288.1	-252.0	0.81
2.1	288.1	-252.0	0.81
2.2	286.6	-250.0	0.80
2.27	286.4	-249.2	0.80
2.35	286.3	-248.4	0.80
2.5	286.3	-247.0	0.82
2.7	283.7	-242.4	0.83
3	273.5	-229.1	0.82
3.2	273.4	-229.0	0.82
3.4	274.2	-229.5	0.82
3.7	275.5	-230.9	0.82
3.8	287.7	-247.8	0.75
4.1	287.2	-245.9	0.76
4.5	282.7	-238.0	0.80

Table S2 (continued). Experimental and Computed ^{15}N NMR Parameters for $[VO^{15}NGlySal(OCH_3)]\cdot(CH_3OH)$ as a Function of V---$OHCH_3$ Distance.

B3LYP/6-311+G			
V-CH_3OH (Å)	**δ_{iso}/ppm**	**δ_σ/ppm (±5)**	**η_σ (±0.05)**
Experiment	**253.2**	**-209.9**	**0.73**
none	282.5	-237.8	0.83
2	287.6	-249.8	0.83
2.1	287.6	-249.8	0.83
2.2	286.3	-247.6	0.82
2.27	286.1	-246.8	0.82
2.35	286.0	246.0	0.83
2.5	285.7	-245.0	0.84
2.7	283.3	-240.6	0.86
3	273.1	-227.5	0.84
3.2	273.1	-227.9	0.84
3.4	274.3	-228.7	0.85
3.7	275.6	-230.1	0.85
3.8	287.6	-246.5	0.77
4.1	287.2	-244.7	0.78
4.5	282.3	-236.8	0.81

Table S3. Experimental and Computed ^{13}C NMR Parameters for [VO^{15}NGlySalbz] and [VO^{15}NGlySal(OCH$_3$)].

[VO^{15}NGlySalbz]					
		BLYP/TZV	BLYP/6-311+G	B3LYP/TZV	B3LYP/6-311+G
Carbon Number*	**Experimental Chemical Shift (ppm)**	**Calculated Chemical Shift (ppm)**	**Calculated Chemical Shift (ppm)**	**Calculated Chemical Shift (ppm)**	**Calculated Chemical Shift (ppm)**
9	176.1	180.6	174.3	192.2	185.5
10	169.6	168.8	163.0	180.6	174.2
1	167.1	166.6	162.1	176.0	171.0
7	165.2	157.7	152.7	170.0	164.6
3	137.7	134.8	131.7	144.3	140.6
5	136.1	131.7	128.0	140.6	136.4
14	134.9	131.5	127.4	140.4	136.0
11**	128.9	131.2	126.2	138.6	134.0
12**	128.9	129.1	125.3	138.1	133.3
13**	128.9	128.7	125.3	136.7	132.9
15**	128.9	127.3	123.8	135.4	131.5
6**	120.9	124.2	119.8	132.1	127.4
16	120.9	123.3	118.9	130.7	126.1
4	120.9	119.1	115.8	126.8	123.1
2	115.2	116.9	112.7	125.1	120.5
8**	61.5	70.6	67.3	75.1	71.7

[VO^{15}NGlySal(OCH$_3$)]					
		BLYP/TZV	BLYP/6-311+G	B3LYP/TZV	B3LYP/6-311+G
Carbon Number	**Experimental Chemical Shift (ppm)**	**Calculated Chemical Shift (ppm)**	**Calculated Chemical Shift (ppm)**	**Calculated Chemical Shift (ppm)**	**Calculated Chemical Shift (ppm)**
9	182.9	183.9	178.9	193.8	188.0
1	168.1	168.7	164.9	176.4	171.9
7**	Missing	158.4	155.0	169.7	165.6
3**	138.8	135.9	133.4	144.1	141.0
5**	137.1	132.2	129.9	140.0	136.9
6	124.6	124.6	120.8	130.2	126.1
4	120.4	121.7	120.0	128.3	125.9
2	119.0	118.8	116.2	126.0	122.9
10	78.9	75.3	73.9	79.4	77.7
8	64.3	68.0	65.5	70.9	68.2

[VO^{15}NGlySal(OCH$_3$)(CH$_3$OH)]					
		BLYP/TZV	BLYP/6-311+G	B3LYP/TZV	B3LYP/6-311+G
Carbon Number	**Experimental Chemical Shift (ppm)**	**Calculated Chemical Shift (ppm)**	**Calculated Chemical Shift (ppm)**	**Calculated Chemical Shift (ppm)**	**Calculated Chemical Shift (ppm)**
9	182.9	183.1	178.2	193.2	187.6
1	168.1	167.6	164.3	175.6	171.5
7**	Missing	158.5	155.4	170.0	166.1
3**	138.8	136.0	133.8	144.5	141.6
5**	137.1	131.8	129.4	139.7	136.7
6	124.6	123.5	120.2	129.4	125.7
4	120.4	121.5	119.5	128.3	125.5
2	119.0	118.5	115.6	125.9	122.5
10	78.9	74.2	73.0	78.1	76.6
8	64.3	68.0	65.8	71.3	68.8
11**	Missing	50.0	48.2	52.5	50.7

*The numbering of the carbon atoms is shown in Figure 1.
**Chemical shifts for these carbons could not be assigned unambiguously due to spectral overlap or missing peaks in the CPMAS spectra.

Table S4. Experimental and Computed (BLYP/TZV) ^{13}C NMR Parameters for $[VO^{15}NGlySal(OCH_3)]\cdot(CH_3OH)$ as a Function of the V---$OHCH_3$ Distance.

Carbon Number*	Experimental Chemical Shift (ppm)	Calculated Chemical Shift (ppm)								
		2.3 Å	**2.7 Å**	**3.0 Å**	**3.2 Å**	**3.4 Å**	**3.7 Å**	**3.8 Å**	**4.1 Å**	**4.5 Å**
9	182.88	185.1	183.2	182.5	182.6	182.9	183.1	188.9	188.2	187.9
1	168.09	171.1	166.4	166.6	166.8	167.3	167.6	170.9	169.7	169.2
7**	N/A	159.7	156.9	157.6	158.2	158.7	158.5	160.5	160.2	160.8
3**	138.80	135.9	133.4	134.7	135.1	135.5	136.0	137.1	136.2	136.3
5**	137.10	133.7	131.1	131.4	131.5	131.8	131.8	134.0	133.3	133.6
6	124.58	126.8	123.3	123.5	123.8	124.5	123.5	125.9	125.5	126.6
4	120.44	121.9	119.1	120.1	120.5	121.0	121.5	123.5	122.5	122.6
2	118.99	119.8	117.0	117.1	117.3	117.8	118.5	120.2	119.5	119.2
10	78.91	80.9	76.8	73.8	73.7	74.1	74.2	76.7	75.6	75.3
8	64.34	64.8	66.3	68.2	68.2	67.9	68.0	70.3	70.4	70.2
11**	N/A	54.5	51.4	49.6	49.7	49.9	50.0	55.4	54.8	54.3

*The numbering of the carbon atoms is shown in Figure 1.
**Chemical shifts for these carbons could not be assigned unambiguously due to spectral overlap or missing peaks in the CPMAS spectra.