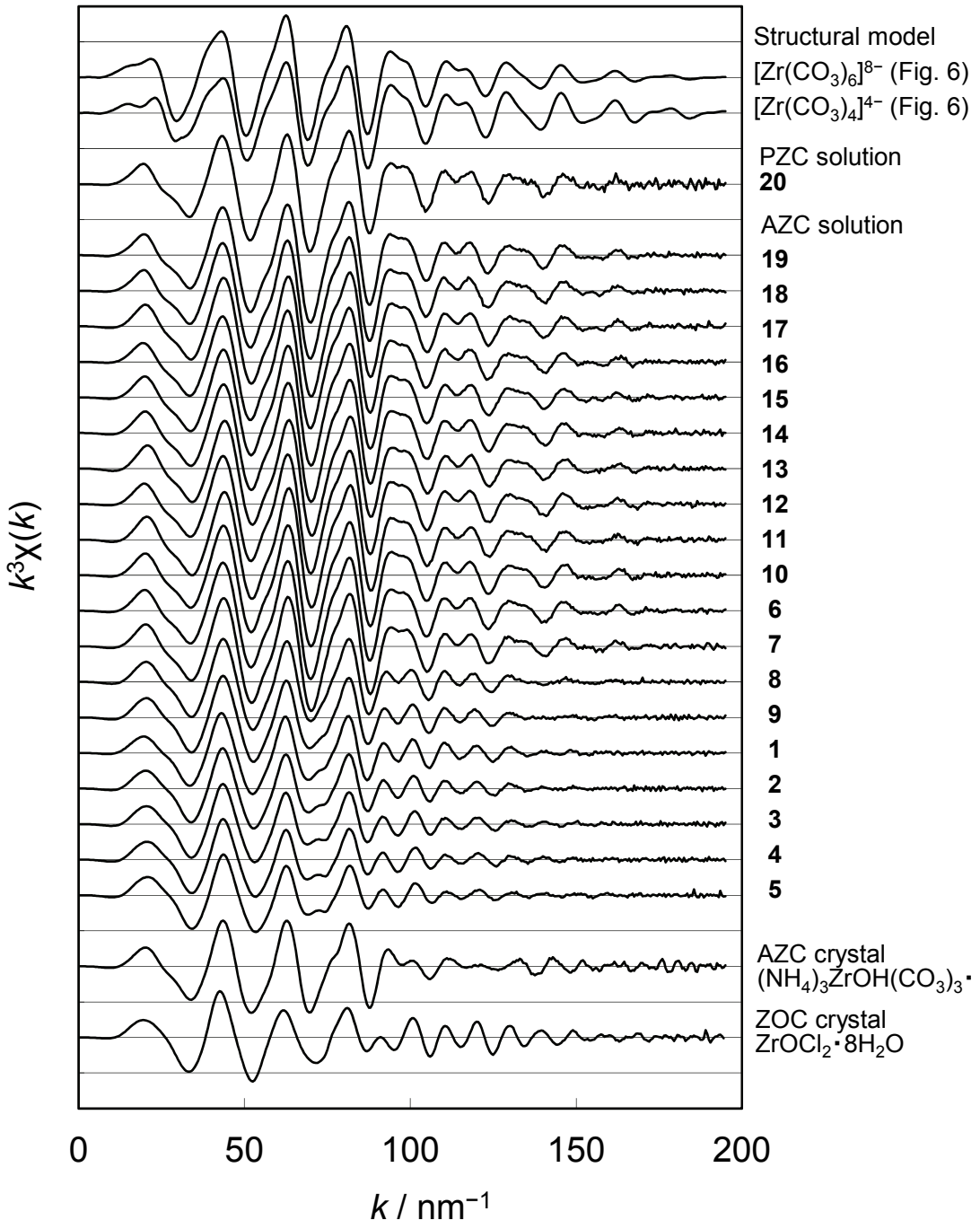

Fig. S1 EXAFS oscillations $k^3\chi(k)$ of AZC and PZC solutions, AZC crystal, ZOC crystal and theoretical spectra corresponding to structural models of $[Zr(CO_3)_4]^{4-}$ and $[Zr(CO_3)_6]^{8-}$.

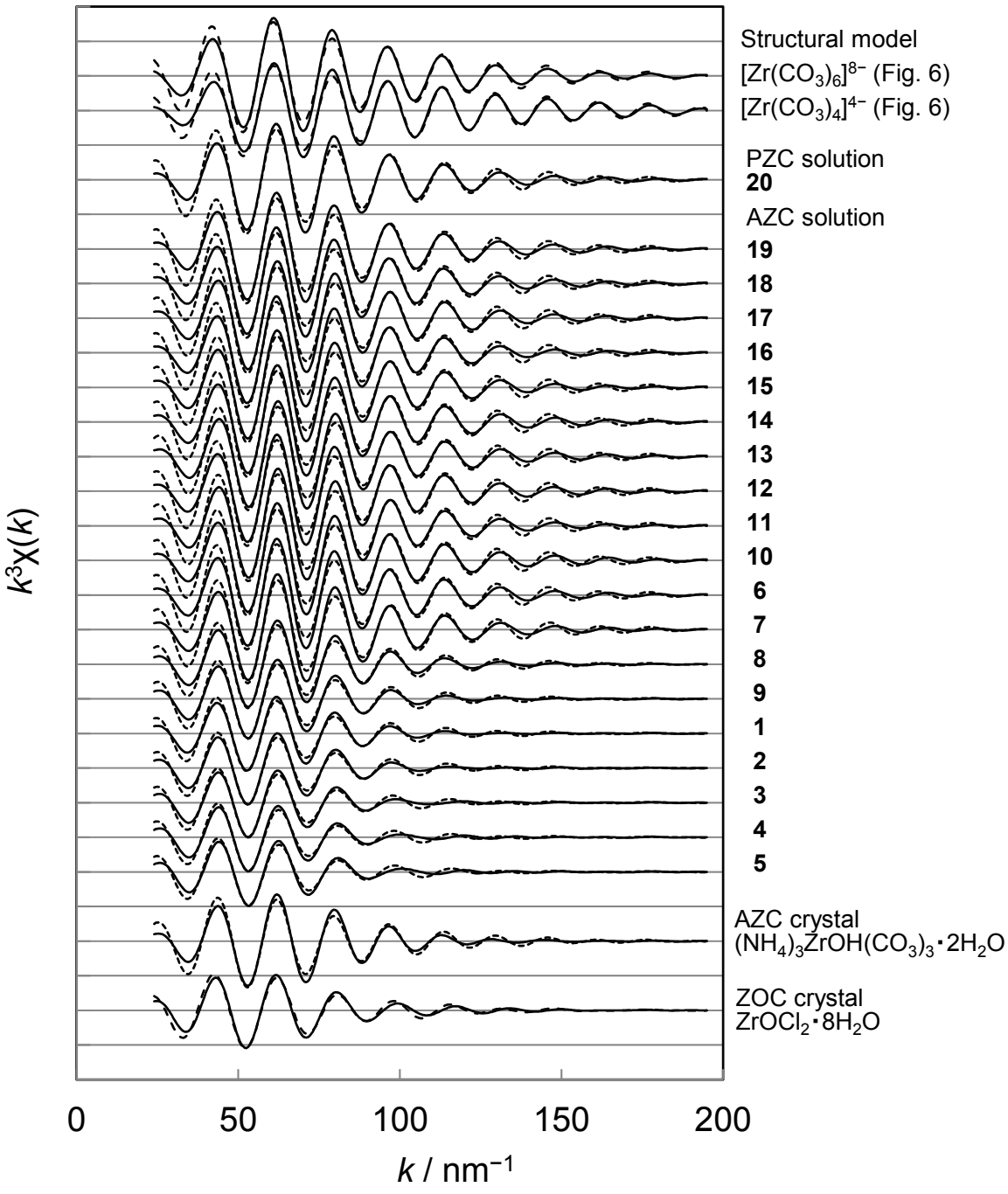

Fig. S2 EXAFS oscillations $k^3\chi(k)$ (solid lines) obtained by inverse-FT of FT spectra shown in Fig. 1 in the r range of 104-227 pm and fitting curves (dashed lines) for calculations of Zr-O coordination parameters in Table S1.

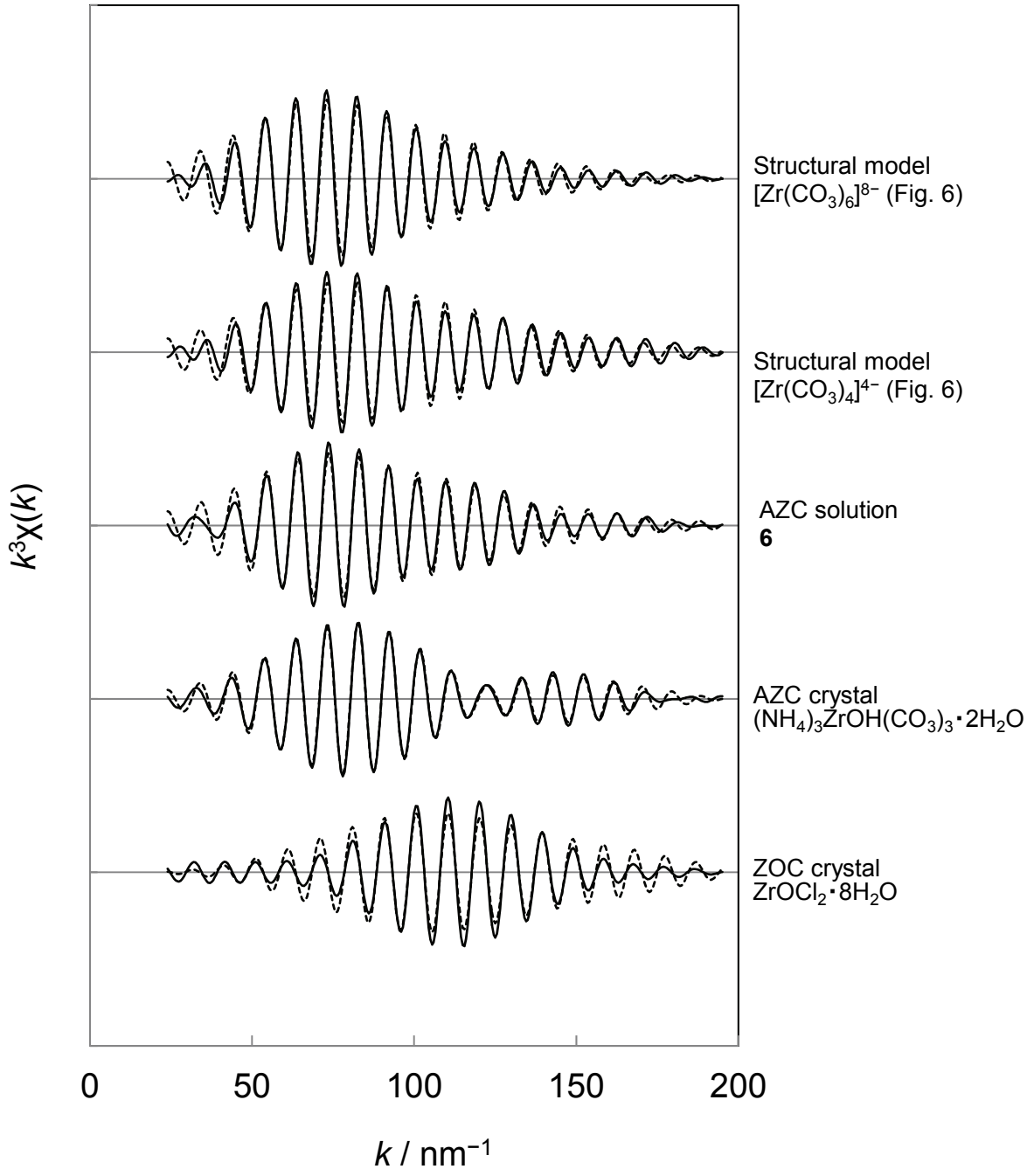

Fig. S3 EXAFS oscillations $k^3\chi(k)$ (solid lines) obtained by inverse-FT of FT spectra shown in Fig. 1 in the r range of 273-384 pm and fitting curves (dashed lines) derived by multi-shell fitting of Zr-Zr coordination and/or multiple scattering paths caused by bidentate carbonate ligand coordinated to zirconium for calculation of their parameters in Table S2.

Table S1 Chemical properties and Zr-O coordination parameters with estimated standard deviation in the bracket obtained by EXAFS analysis of AZC solutions, PZC solution, AZC crystal, ZOC crystal and theoretical spectra of the structural models in Fig. 1.

No.	[Zr] / M	[carbonate] / M	[ammonium] / M	pH	$N_{Zr\text{-}O}$	$r_{Zr\text{-}O}$ / pm	E_0 / eV	ΔE_0 / eV	σ / pm
1	0.1	0.3	0.3	8.3	7.2 (0.8)	220.8 (1.1)	18001.2	2.9 (1.6)	9.7 (1.3)
2	0.1	0.3	0.6	9.3	7.3 (0.8)	220.3 (1.1)	18000.2	3.6 (1.6)	10.1 (1.4)
3	0.1	0.3	1.0	9.7	7.2 (0.9)	219.3 (1.2)	18000.0	3.0 (1.7)	10.6 (1.5)
4	0.1	0.3	1.6	10.0	7.2 (0.9)	218.6 (1.2)	17999.9	2.5 (1.8)	10.8 (1.5)
5	0.1	0.3	2.0	10.2	7.1 (0.9)	218.1 (1.2)	17999.8	2.4 (1.8)	10.8 (1.5)
6	0.1	0.6	0.6	7.9	8.8 (0.8)	221.3 (0.8)	18000.8	3.4 (1.5)	7.5 (1.0)
7	0.1	0.6	1.0	9.2	8.7 (0.8)	221.1 (0.8)	17999.7	4.0 (1.4)	7.6 (1.0)
8	0.1	0.6	1.6	9.6	7.8 (0.8)	221.1 (0.9)	17999.7	4.5 (1.4)	8.8 (1.2)
9	0.1	0.6	2.0	9.8	7.5 (0.8)	220.8 (1.0)	17999.6	4.3 (1.5)	9.4 (1.3)
10	0.1	1.0	1.0	7.8	8.8 (0.8)	221.1 (0.7)	18000.5	3.6 (1.4)	7.4 (1.0)
11	0.1	1.0	1.6	9.0	9.0 (0.9)	221.3 (0.7)	17999.3	4.9 (1.4)	7.6 (1.0)
12	0.1	1.0	2.0	9.4	8.7 (0.8)	221.1 (0.7)	18000.7	3.2 (1.5)	7.4 (1.0)
13	0.1	1.0	2.6	9.6	8.6 (0.8)	221.1 (0.7)	17999.0	5.0 (1.4)	7.5 (1.0)
14	0.1	1.6	1.6	7.8	8.8 (0.8)	221.1 (0.7)	18000.3	3.6 (1.4)	7.5 (1.0)
15	0.1	1.6	2.0	8.4	8.9 (0.8)	221.2 (0.8)	18000.4	3.8 (1.4)	7.5 (1.0)
16	0.1	2.0	2.0	7.8	8.8 (0.8)	221.1 (0.8)	18001.3	2.7 (1.5)	7.5 (1.0)
17	0.1	2.0	2.6	8.4	8.8 (0.8)	221.1 (0.7)	18000.1	3.8 (1.4)	7.4 (1.0)
18	0.5	3.0	3.0	8.6	8.8 (0.8)	221.4 (0.8)	18002.8	2.9 (1.5)	7.5 (1.0)
19	0.8	4.8	4.8	8.8	8.7 (0.8)	221.4 (0.8)	18002.8	3.0 (1.5)	7.5 (1.0)
No.	[Zr] / M	[carbonate] / M	[potassium] / M	pH	$r_{Zr\text{-}O}$ / pm	$r_{Zr\text{-}O}$ / pm	E_0 / eV	ΔE_0 / eV	σ / pm
20	0.08	0.48	0.66	9.2	8.7 (0.8)	221.3 (0.8)	18002.7	2.6 (1.5)	7.5 (1.0)
AZC crystal $(NH_4)_3ZrOH(CO_3)_3\cdot 2H_2O$					8.3 (0.8)	222.3 (0.9)	17999.7	5.2 (1.4)	8.7 (1.2)
Zirconium oxychloride $ZrOCl_2\cdot 8H_2O$					7.4 (0.8)	217.5 (1.1)	18006.6	-2.1 (1.8)	9.9 (1.4)
Structural model $[Zr(CO_3)_4]^{4-}$					6.6 (0.6)	221.5 (0.6)	17998.0	-0.7 (1.4)	5.9 (0.9)
Structural model $[Zr(CO_3)_6]^{8-}$					8.8 (0.8)	221.4 (0.7)	17998.0	-1.3 (1.5)	7.0 (1.0)

Table S2 Chemical properties and parameters derived by multi-shell fitting of Zr-Zr coordination and/or multiple scattering paths caused by bidentate carbonate ligand coordinated to zirconium with estimated standard deviation in the bracket by EXAFS analysis of AZC solution, AZC crystal, ZOC crystal and theoretical spectra of the structural models in Fig. 1.

No.	[Zr] / M	[carbonate] / M	[ammonium] / M	pH	Coordination or scattering path	N	r / pm	E_0 / eV	ΔE_0 / eV	σ / pm
6	0.1	0.3	0.3	8.3	Zr-O*-C-Zr (or Zr-C-O*-Zr)[a]	10.9 (5.1)	389.1 (0.9)	18000.8	2.4 (2.1)	7.4 (1.1)
					Zr-C-O*-C-Zr[a]	5.4[b]	389.1[c]		-1.1 (5.9)	7.4[c]
AZC crystal $(NH_4)_3ZrOH(CO_3)_3\cdot 2H_2O$					Zr-Zr	1.4 (0.5)	350.9 (1.5)	17999.7	1.0 (4.1)	7.5 (1.6)
					Zr-O*-C-Zr (or Zr-C-O*-Zr)[a]	5.4 (6.3)	391.6 (2.1)		3.1 (4.0)	7.1 (2.9)
					Zr-C-O*-C-Zr[a]	2.7[b]	391.6[c]		1.1 (13.4)	7.1[c]
Zirconium oxychloride $ZrOCl_2\cdot 8H_2O$					Zr-Zr	1.4 (0.2)	356.1 (0.6)	18006.6	-3.0 (1.5)	6.2 (0.8)
Structural model $[Zr(CO_3)_4]^{4-}$					Zr-O*-C-Zr (or Zr-C-O*-Zr)[a]	13.8 (2.4)	389.2 (0.6)	17998.0	0.5 (1.6)	7.4 (0.7)
					Zr-C-O*-C-Zr[a]	6.9[b]	389.2[c]		-6.1 (3.0)	7.4[c]
Structural model $[Zr(CO_3)_6]^{8-}$					Zr-O*-C-Zr (or Zr-C-O*-Zr)[a]	18.0 (3.0)	390.0 (0.6)	17998.0	0.7 (1.5)	8.5 (0.8)
					Zr-C-O*-C-Zr[a]	9.0[b]	390.0[c]		-5.4 (2.7)	8.5[c]

[a] The paths referred to the model in Fig. 2 and were represented by atomic labels in it, [b] A constraint condition, for which the values were a half of those of the path of Zr-O*-C-Zr,, was applied. [c] A constraint condition, for which the values were equal to those of Zr-O*-C-Zr., was applied.

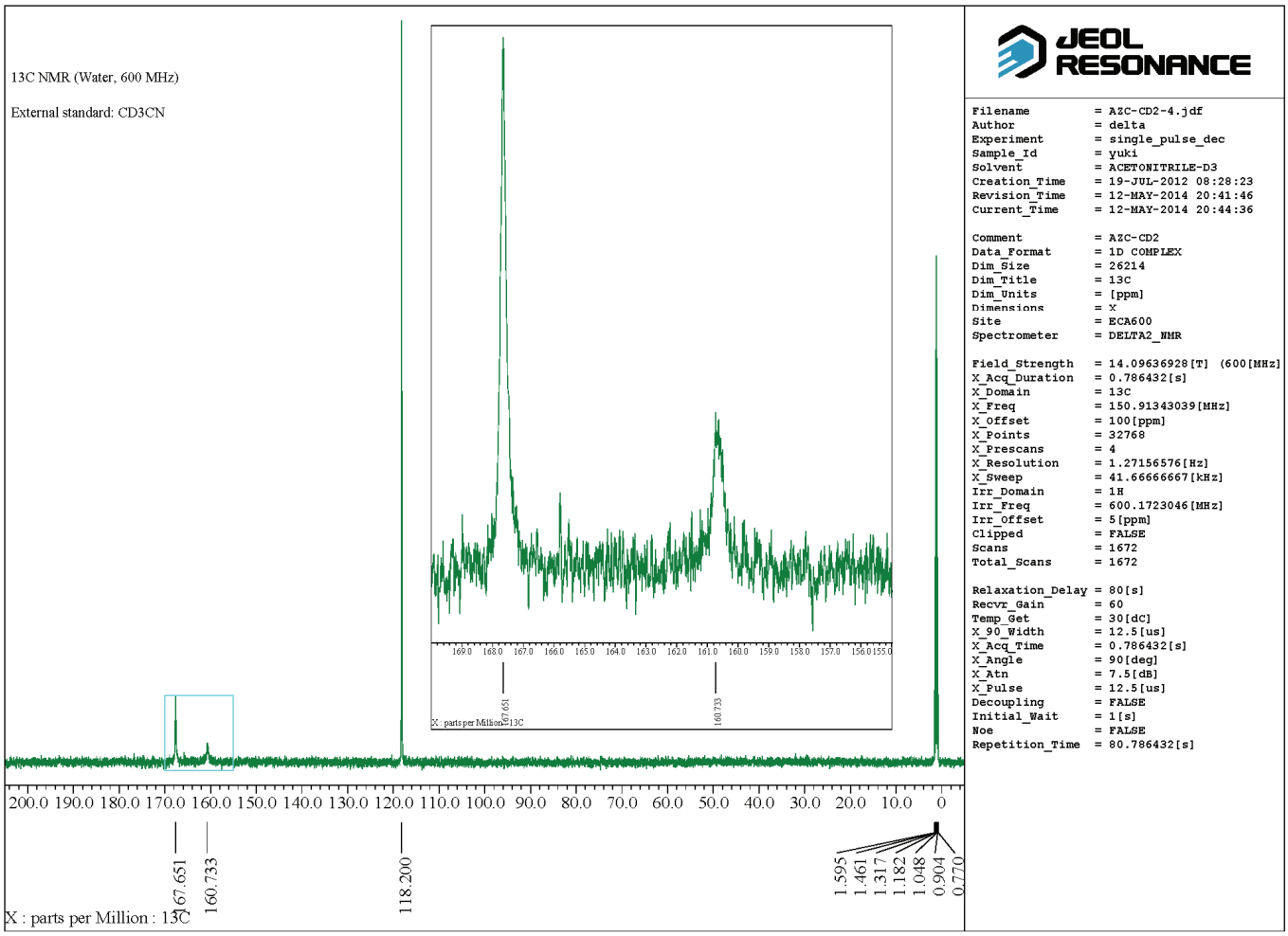

Fig. S4 ^{13}C NMR spectrum of ammonium zirconium carbonate solution in which [Zr] = 0.1 M, [ammonium] = 0.6 M and [carbonate] = 0.6 M (sample **6**).

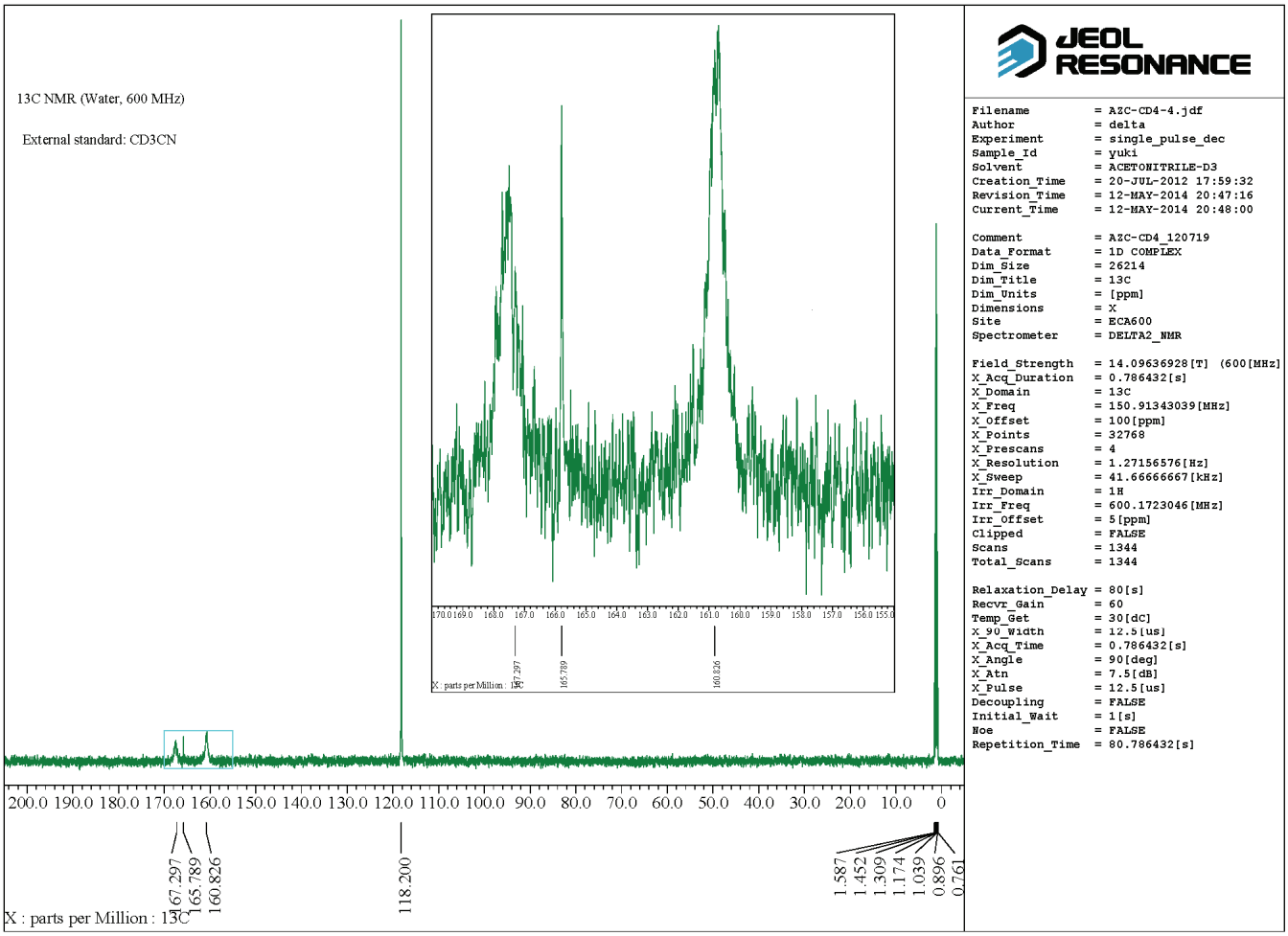

Fig. S5 ^{13}C NMR spectrum of ammonium zirconium carbonate solution in which [Zr] = 0.1 M, [ammonium] = 1.0 M and [carbonate] = 1.0 M (sample **10**).

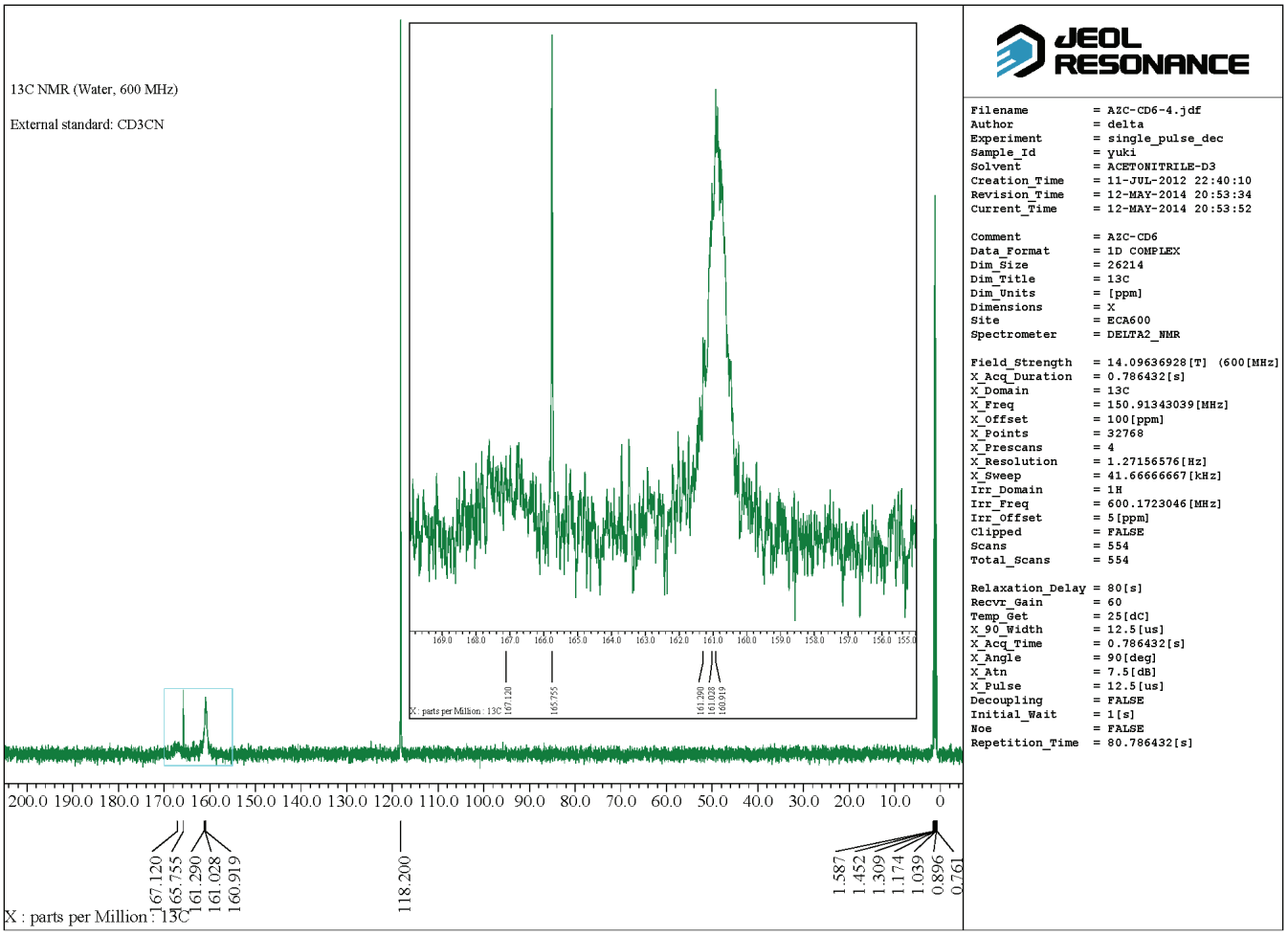

Fig. S6 ^{13}C NMR spectrum of ammonium zirconium carbonate solution in which [Zr] = 0.1 M, [ammonium] = 1.6 M and [carbonate] = 1.6 M (sample **14**).