

# Speciation and structure of tin(II) in hyper-alkaline aqueous solution

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## Electronic Supplementary Information

**Table S1.** Raman spectroscopic parameters of alkaline solutions containing Sn(II). The spectrum of the background solution has been subtracted.

$C_{\text{Sn(II)}}$ (M)	$C_{\text{NaOH}}$ (M)	Band at $\sim 430 \text{ cm}^{-1}$			Band at $\sim 490 \text{ cm}^{-1}$		
		$\sigma^a$ ( $\text{cm}^{-1}$ )	FWHH <sup>b</sup> ( $\text{cm}^{-1}$ )	I <sup>c</sup> (a.u.)	$\sigma^a$ ( $\text{cm}^{-1}$ )	FWHH <sup>b</sup> ( $\text{cm}^{-1}$ )	I <sup>c</sup> (a.u.)
0.10	4.0	434.9	55	0.81	486.2	35	0.30
0.15	4.0	433.4	61	1.44	491.1	50	0.83
0.20	4.0	433.4	56	1.67	487.7	43	0.64
0.25	4.0	433.7	62	2.40	489.8	45	1.08
0.10	8.0	438.7	69	0.80	496.7	53	0.68
0.15	8.0	440.5	69	1.72	495.3	35	0.42
0.25	8.0	437.6	54	1.99	492.6	58	1.36
0.10	4.0 <sup>d</sup>	430.6	70	1.00	490.2	52	0.63
0.20	4.0 <sup>d</sup>	432.9	68	1.81	489.9	53	1.02
0.10	$\sim 14^d$	448	66	1.17	505	48	0.65

<sup>a</sup> Raman shift

<sup>b</sup> Full bandwidth at half height

<sup>c</sup> Peak intensity

<sup>d</sup> KOH instead of NaOH

**Table S2.** Mössbauer parameters obtained for rapidly frozen aqueous alkaline solutions containing Sn(II). Measurements were performed at 78 K.

$C_{\text{Sn(II)}}$ (M)	$C_{\text{NaOH}}$ (M)	$\delta$ (mm/s)	$\Delta$ (mm/s)
<b>0.01</b>	0.1	2.60	2.08
<b>0.1</b>	1.0	2.59	2.03
<b>0.1</b>	4.0	2.58	2.01
<b>0.2</b>	4.0	2.59	2.00
<b>0.2</b>	4.0	2.47	1.87
<b>0.2</b>	12.0	2.55	2.02
<b>0.5</b>	8.0	2.61	1.83

$\delta$  and  $\Delta$  denote the isomer shift and quadrupole splitting, respectively. The standard deviations are  $\pm 0.03$  mm/s and  $\pm 0.06$  mm/s for  $\delta$  and  $\Delta$ , respectively.

**Table S3.** Summary of solid state structures containing trichlorostannate,  $[SnCl_3]^-$  or tetrachlorostannate,  $[SnCl_4]^{2-}$  complexes. The list is based on the data collected from the Inorganic Crystal Structure Database (ICSD) and the Cambridge Structural Database (CSD).

**Trichlorostannate(II)**

ICSD/CSD code	$d_{Sn-Cl}$	Reference
PECOTB20	2.430 Å	Stalick, J. K.; Corfield, P. W. R; Meek, D. W. <i>Inorg. Chem.</i> <b>1973</b> , <i>12</i> , 1668.
PPECOT20	2.445 Å	Stalick, J. K.; Corfield, P. W. R; Meek, D. W. <i>Inorg. Chem.</i> <b>1973</b> , <i>12</i> , 1668.
DOWKIJ	2.453 Å	Fong, L. K.; Fox, J. R.; Foxman, B. M.; Cooper, N. J. <i>Inorg. Chem.</i> <b>1986</b> , <i>25</i> , 1880.
BIWLUP	2.466 Å	Hernandez-Molina, R.; Kalinina, I. V.; Abramov, P. A.; Sokolov, M. N.; Virovets, A. V.; Platas J. G.; Llusar, R.; Polo, V.; Vicent, C.; Fedin, V. P. <i>Inorg. Chem.</i> <b>2008</b> , <i>47</i> , 306.
SIGMEA	2.467 Å	Veith, M.; Godicke, B.; Huch, V. Z. <i>Anorg. Allg. Chem.</i> <b>1989</b> , <i>579</i> , 99.
VOGRAK	2.467 Å	Balch, A. L.; Neve, F.; Olmstead, M. M. <i>Inorg. Chem.</i> <b>1991</b> , <i>30</i> , 3395.
240910	2.468 Å	Szafranski, M.; Ståhl, K. <i>J. Solid State Chem.</i> <b>2007</b> , <i>180</i> , 2209-2215.
XETZUS	2.471 Å	Muller, U.; Mronga, N.; Schumacher, C.; Dehnicke, K. Z. <i>Naturforsch., Teil B</i> <b>1982</b> , <i>37</i> , 1122.
NAKPUK	2.474 Å	Constantine, S. P.; De Lima, G. M.; Hitchcock, P. B.; Keates, J. M.; Lawless, G. A. <i>Chem. Commun.</i> <b>1996</b> , 2337.
LAQVUU	2.480 Å	Faure, J.-L.; Gornitzka, H.; Reau, R.; Stalke, D.; Bertrand, G. <i>Eur. J. Inorg. Chem.</i> <b>1999</b> , 2295.
DUSWOD	2.481 Å	Drew, M. G. B.; Nicholson, D. G. <i>J. Chem. Soc., Dalton Trans.</i> <b>1986</b> , 1543.
SIGNIF	2.486 Å	Veith, M.; Godicke, B.; Huch, V. Z. <i>Anorg. Allg. Chem.</i> <b>1989</b> , <i>579</i> , 99.
ENCOSN	2.488 Å	Haupt, H. J.; Huber, F.; Preut, H. Z. <i>Anorg. Allg. Chem.</i> <b>1976</b> , <i>422</i> , 255.
KAYJOJ	2.500 Å	Hough, E.; Nicholson, D. G.; Vasudevan, A. K. <i>J. Chem. Soc., Dalton Trans.</i> <b>1989</b> , 2155.
170096	2.505 Å	Halfpenny, J. <i>Acta Crystallogr., Sect. C</i> <b>1996</b> , <i>52</i> , 340-342.
GIYGOK	2.507 Å	Kuhn, N.; Fawzi, R.; Kotowski, H.; Steimann. M. Z. <i>Kristallogr.-New Cryst. Struct</i> <b>1998</b> , <i>213</i> , 435.
KAHWAR	2.515 Å	Veith, M.; Huch, V.; Lisowsky, R.; Hobein, P. Z. <i>Anorg. Allg. Chem.</i> <b>1989</b> , <i>569</i> , 43.
14199	2.523 Å	Poulsen, F. R.; Rasmussen, S. E. <i>Acta Chem. Scand.</i> <b>1970</b> , <i>24</i> , 150-156.
BZSACS	2.527 Å	Elder, R. C.; Heeg, M. J.; Deutsch, E. <i>Inorg. Chem.</i> <b>1978</b> , <i>17</i> , 427.
GEHTUI	2.542 Å	Veith, M.; Jarczyk, M.; Huch, V. <i>Chem. Ber.</i> <b>1988</b> , <i>121</i> , 347.
30171	2.559 Å	Harrison, P. G.; Haylett, B. J.; King, T. J. <i>Inorg. Chim. Acta</i> <b>1983</b> , <i>75</i> , 265-270.
110664	2.567 Å	Yamada, K.; Kuranaga, Y.; Ueda, K.; Goto, S.; Okuda, T.; Furukawa, Y. <i>Bull. Chem. Soc. Jpn.</i> <b>1998</b> , <i>71</i> , 127-134.
14219	2.571 Å	Kamenar, B.; Grdenic, D. <i>J. Inorg. Nucl. Chem.</i> <b>1962</b> , <i>24</i> , 1039-1045.

1363	2.603 Å	Haupt, H. J.; Huber, F.; Sandbute, H. W. Z. <i>Anorg. Allgem. Chem.</i> <b>1977</b> , <i>435</i> , 191-196.
32593	2.605 Å	Golic, L.; Kaucic, V.; Trontelj, Z. <i>Docum. Chem. Jugoslav. Vestnik Sloven. Kemi. Drustva</i> <b>1979</b> , <i>26</i> , 425-434.
415711	2.610 Å	Abraham, I.; Demetriou, D. Z.; Vordemvenne, E.; Mustarde, K.; Benoit, D. M. <i>Polyhedron</i> <b>2006</b> , <i>25</i> , 996-1002.
110663	2.637 Å	Yamada, K.; Kuranaga, Y.; Ueda, K.; Goto, S.; Okuda, T.; Furukawa, Y. <i>Bull. Chem. Soc. Jpn.</i> <b>1998</b> , <i>71</i> , 127-134.
<b>Average</b>	<b>2.513 Å/27 structures</b>	

**Tetrachlorostannate(II)**

VIZJET	2.634 Å	Sokol, V. I.; Vasilenko, T. G.; Porai-Koshits, M. A.; Molodkin, A. K.; Vasnin, S. V. <i>Zh. Neorg. Khim.</i> <b>1990</b> , <i>35</i> , 2017.
<b>Average</b>	<b>2.634 Å/1 structure</b>	

**Table S4** The oxygen coordinated tin(II) structures used for determine the coordination number – Sn-O bond distance relationship for coordination numbers = 2, 3, 4, 5, 6, 8. The list is based on the data collected from the Inorganic Crystal Structure Database (ICSD) and the Cambridge Structural Database (CSD);  $N$  = coordination number; references marked in red text are omitted from the mean bond distance and angle.

$N$	CSD code	$d_{\text{Sn}-\text{O}}$	$\angle \text{O-Sn-O}$	Reference
2	BOSSIM	1.964 Å	99.5 °	Nembenna, S.; Singh, S.; Jana, A.; Roesky, H. W.; Ying Yang, Hongqi Ye; Ott, H.; Stalke, D. <i>Inorg. Chem.</i> <b>2009</b> , <i>48</i> , 2273.
2	PAQHIY	1.992 Å	95.6 °	Hascall, T.; Rheingold, A. L.; Guzei, I.; Parkin, G. <i>Chem. Commun.</i> <b>1998</b> , 101.
2	HEBXOB	2.024 Å	88.8 °	Barnhart, D. M.; Clark, D. L.; Watkin, J. G. <i>Acta Crystallogr., Sect.C</i> <b>1994</b> , <i>50</i> , 702.
2	HEBXOB01	2.026 Å	89.0 °	Boyle, T. J.; Doan, T. Q.; Steele, L. A. M.; Applett, C.; Hoppe, S. M.; Hawthorne, K.; Kalinich, R. M.; Sigmund, W. M. <i>Dalton Trans.</i> <b>2012</b> , <i>41</i> , 9349.
2	LIXLUA	2.041 Å	87.3 °	Dickie, D. A.; MacIntosh, I. S.; Ino, D. D.; Qi He; Labeoden, O. A.; Jennings, M. C.; Schatte, G.; Walsby, C. J.; Clyburne, J. A. C. <i>Can. J. Chem.</i> <b>2008</b> , <i>86</i> , 20.
2	PEBVIC	2.047 Å	92.2 °	Stanciu, C., Richards, A. F.; Stender, M.; Olmstead, M. M.; Power, P. P <i>Polyhedron</i> <b>2006</b> , <i>25</i> , 477.

2	NINSIN	2.069 Å	89.4 °	Hascall, T.; Keliang Pang; Parkin, G. <i>Tetrahedron</i> <b>2007</b> , <i>63</i> , 10826.	
2	JOQBOG	2.104 Å	73.0 °	McBurnett, B. G.; Cowley A. H. <i>Chem. Commun.</i> <b>1999</b> , <i>17</i> .	
<b>Average</b>		<b>2.023 Å/7 structures</b>			
2	DASJEM				
2	TBMGEB	Fjeldberg, T.; Hitchcock, P. B.; Lappert, M. F.; Smith, S. J.; Thorne, A. J. <i>Chem. Commun.</i> <b>1985</b> , <i>939</i> . Cetinkaya, B.; Gumrukcu, I.; Lappert, M. F.; Atwood, J. L.; Rogers, R. D.; Zaworotko, M. J. <i>J. Am. Chem. Soc.</i> <b>1980</b> , <i>102</i> , 2088.			
3	Na <sub>4</sub> [Sn(OH) <sub>3</sub> ] <sub>2</sub> - [Sn <sub>2</sub> O(OH) <sub>4</sub> ]	35420	2.080 Å	88.1 °	von Schnering, H.G.; Nesper, R.; Pelshenke, H. <i>Z. Anorg. Allgem. Chem.</i> <b>1983</b> , <i>499</i> , 117-129
3	Na <sub>4</sub> [Sn(OH) <sub>3</sub> ] <sub>2</sub> - [Sn <sub>2</sub> O(OH) <sub>4</sub> ]	35420	2.066 Å	89.3 °	von Schnering, H.G.; Nesper, R.; Pelshenke, H. <i>Z. Anorg. Allgem. Chem.</i> <b>1983</b> , <i>499</i> , 117-129
3	Sn <sub>3</sub> O(OH) <sub>2</sub> (SO <sub>4</sub> )	4294	2.122 Å	89.2 °	Grimvall, S. <i>Acta Chem. Scand., Ser. A</i> <b>1975</b> , <i>29</i> , 590-598.
3	Sn <sub>3</sub> O(OH) <sub>2</sub> (SO <sub>4</sub> )	15778	2.127 Å	89.6 °	Davies, C. G.; Donaldson, J. D.; Laughlin, D. R.; Howie, R. A.; Beddoes, R. <i>J. Chem. Soc., Dalton Trans.</i> , <b>1975</b> , 2241-2244.
3	Sn <sub>3</sub> O(OH)(PO <sub>4</sub> )	23339	2.135 Å	83.8 °	Jordan, T. H.; Dickens, B.; Schroeder, L. W.; Brown, W. E. <i>Inorg. Chem.</i> <b>1980</b> , <i>19</i> , 2551-2556.
3	Sn <sub>3</sub> O(OH)(PO <sub>4</sub> )	23339	2.171 Å	84.8 °	Jordan, T. H.; Dickens, B.; Schroeder, L. W.; Brown, W. E. <i>Inorg. Chem.</i> <b>1980</b> , <i>19</i> , 2551-2556.
<b>Average</b>		<b>2.117 Å</b>	<b>87.5 °/6 structures</b>		
4	SnO	26597	2.211 Å	89.2 °	Moore, W. J.; Pauling, L. <i>J. Am. Chem. Soc.</i> <b>1941</b> , <i>63</i> , 1392-1394.
4	SnO	15516	2.219 Å	88.9 °	Izumi, F. <i>J. Solid State Chem.</i> <b>1981</b> , <i>38</i> , 381-385.
4	SnO	41954	2.222 Å	88.8 °	Moreno, M. S.; Mercader, R. C. <i>Phys. Rev. B</i> <b>1994</b> , <i>50</i> , 9875-9881.
4	SnO	16481	2.224 Å	88.8 °	Pannetier, J.; Denes, G. <i>Acta Crystallogr., Sect. B</i> <b>1980</b> , <i>36</i> , 2763-2765.

4	SnO	185350	2.224 Å	88.7 °	Allen, J. P.; Scanlon, D. O.; Parker, S. C.; Watson, G. W. <i>J. Phys. Chem. C</i> <b>2011</b> , <i>115</i> , 19916-19924.
4	Sn <sub>3</sub> O(OH)(PO <sub>4</sub> )	23339	2.246 Å	91.6 °	Jordan, T. H.; Dickens, B.; Schroeder, L. W.; Brown, W. E. <i>Inorg. Chem.</i> <b>1980</b> , <i>19</i> , 2551-2556.
4	Sn <sub>3</sub> O(OH) <sub>2</sub> O(SO <sub>4</sub> )	15778	2.273 Å	89.3 °	Davies, C. G.; Donaldson, J. D.; Laughlin, D. R.; Howie, R. A.; Beddoes, R. <i>J. Chem. Soc., Dalton Trans.</i> , <b>1975</b> , 2241-2244.

**Average**                                   **2.224 Å**   **89.3 °/6 structures**

<i>N</i>	CSD code	<i>d</i> <sub>Sn-O</sub>	∠O-Sn-O	Reference
3	FEKTOF	2.085 Å	85.0 °	Veith, M.; Ehses, M.; Huch, V. <i>New J. Chem.</i> <b>2005</b> , <i>29</i> , 154-164.
3	DUVNIR	2.092 Å	88.8 °	Veith, M.; Rosler, R. Z. <i>Naturforsch., Teil B</i> <b>1986</b> , <i>41</i> , 1071.
3	DEPQEY	2.093 Å	86.6 °	Ramaswamy, P.; Natarajan, S. <i>Eur. J. Inorg. Chem.</i> <b>2006</b> , 3463-3471.
3	DUVNOX	2.094 Å	87.1 °	Veith, M.; Rosler, R. Z. <i>Naturforsch., Teil B</i> <b>1986</b> , <i>41</i> , 1071.
3	FEKTUL	2.096 Å	85.5 °	Veith, M.; Ehses, M.; Huch, V. <i>New J. Chem.</i> <b>2005</b> , <i>29</i> , 154-164.
3	DASHUA	2.101 Å	79.7 °	Fjeldberg, T.; Hitchcock, P. B.; Lappert, M. F.; Smith, S. J.; Thorne, A. J. <i>J. Chem. Soc., Chem. Commun.</i> <b>1985</b> , 939-941.
3	JIYPIQ	2.102 Å	79.3 °	Ayyappan, S.; Bu, X.; Cheetham, A. K.; Natarajan, S.; Rao, C. N. R <i>Chem. Commun.</i> <b>1998</b> , 2181-2182.
3	DUVNOX	2.106 Å	86.8 °	Veith, M.; Rosler, R. Z. <i>Naturforsch., Teil B</i> <b>1986</b> , <i>41</i> , 1071.
3	JOTHOP	2.111 Å	86.9 °	Natarajan, S.; Eswaramoorthy, M.; Cheetham, A. K.; Rao, C. N. R. <i>Chem. Commun.</i> <b>1998</b> , 1561-1562.
3	BIFJOQ	2.115 Å	86.0 °	Duchateau, R.; Dijkstra, T. W.; Severn, J. R.; van Santen, R. A.; Korobkov, I. V. <i>Dalton Trans.</i> <b>2004</b> , 2677-2682.
3	GIVDOE	2.116 Å	86.5 °	Ayyappan, S.; Cheetham, A. K.; Natarajan, S.; Rao, C. N. R. <i>J. Solid State Chem.</i> <b>1998</b> , <i>139</i> , 207-210.
3	JOQBEW	2.126 Å	80.9 °	McBurnett, B. G.; Cowley, A. H. <i>Chem. Commun.</i> <b>1999</b> , 17-18.
3	JOQBEW	2.139 Å	80.0 °	McBurnett, B. G.; Cowley, A. H. <i>Chem. Commun.</i> <b>1999</b> , 17-18.
3	KAFHEE	2.150 Å	76.0 °	Smith, G. D.; Fanwick, P. E.; Rothwell, I. P. <i>Inorg. Chem.</i> <b>1989</b> , <i>28</i> , 618-620.

3	BIDWIV	2.159 Å	84.9 °	Reuter, H. Z. <i>Kristallogr.-New Cryst. Struct.</i> <b>2004</b> , <i>219</i> , 109-110.
3	COHVEA	2.184 Å	79.4 °	Arifin, A.; Filmore, E. J.; Donaldson, J. D.; Grimes, S. M. <i>J. Chem. Soc., Dalton Trans.</i> <b>1984</b> , 1965-1968.
<b>Average:</b>		<b>2.112 Å</b>	<b>84.0 °</b>	<b>/15 structures</b>

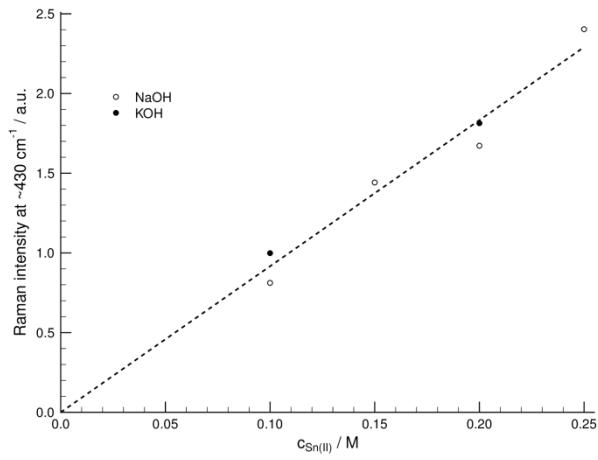
N	CSD code	$d_{\text{Sn-O}}$	$\angle \text{O-Sn-O}$	Reference
4	SUXLAY	2.195 Å	89.0 °	Barret, M. C.; Mahon, M. F.; Molloy, K. C., Steed, J. W.; Wright, P. <i>Inorg. Chem.</i> <b>2001</b> , <i>40</i> , 4384-4388.
4	YERBON	2.199 Å	97.2 °	Ionkin, A. S.; Marshall, W. J.; Fish, B. M. <i>Organometallics</i> <b>2006</b> , <i>25</i> , 4170-4178.
4	PBONSN	2.216 Å	94.2 °	Ewings, P. F. R.; Harrison, P. G.; King, T. J. <i>J. Chem. Soc., Dalton Trans.</i> <b>1975</b> , 1455-1458.
4	SIHQOP	2.221 Å	90.4 °	Ayyappan, S.; Cheetham, A. K.; Natarajan, S.; Rao, C. N. R. <i>Chem. Mater.</i> <b>1998</b> , <i>10</i> , 3746-3755.
4	WIDCAN	2.221 Å	92.2 °	Pettinari, C.; Marchetti, F.; Cingolani, A.; Marciante, C.; Spagna, R.; Colapietro, M. <i>Polyhedron</i> <b>1994</b> , <i>13</i> , 939-950.
4	XEXSUP	2.222 Å	83.5 °	Piskunov, A. V.; Lado, A. V.; Fukin, G. K.; Baranov, E. V.; Abakumova, L. G.; Cherkasov, V. K.; Abakumov, G. A. <i>Heteroat. Chem.</i> <b>2006</b> , <i>17</i> , 481-490.
4	SUXKUR	2.225 Å	91.9 °	Barret, M. C.; Mahon, M. F.; Molloy, K. C., Steed, J. W.; Wright, P. <i>Inorg. Chem.</i> <b>2001</b> , <i>40</i> , 4384-4388.
4	ABIBIX	2.230 Å	91.3 °	Pettinari, C.; Marchetti, F.; Pettinari, R.; Cingolani, A.; Rivarola, E.; Phillips, C.; Tanski, J.; Rossi, M.; Caruso, F. <i>Eur. J. Inorg. Chem.</i> , <b>2004</b> , 3484-3497.
4	DPPRSN	2.231 Å	90.7 °	Uchida, T.; Kozawa, K.; Obara, H. <i>Acta Crystallogr., Sect. B</i> <b>1977</b> , <i>33</i> , 3227-3229.
4	KSNOXL	2.233 Å	88.9 °	Christie, A. D.; Howie, R.A.; Moser, W. <i>Inorg. Chim. Acta</i> <b>1979</b> , <i>36</i> , L447-L448.
4	AGEBIX	2.240 Å	98.0 °	Boyle, T. J.; Alam, T. M.; Rodriguez, M. A.; Zechmann, C. A. <i>Inorg. Chem.</i> <b>2002</b> , <i>41</i> , 2574-2582.
4	XEXSUP	2.247 Å	87.9 °	Piskunov, A. V.; Lado, A. V.; Fukin, G. K.; Baranov, E. V.; Abakumova, L. G.; Cherkasov, V. K.; Abakumov, G. A. <i>Heteroat. Chem.</i> <b>2006</b> , <i>17</i> , 481-490.
4	NOWWAX	2.256 Å	90.3 °	Deacon, P. R.; Mahon, M. F.; Molloy, K. C.; Waterfield, P. C. <i>J. Chem. Soc., Dalton Trans.</i> <b>1997</b> , 3705-3712.
4	XEXSUP	2.273 Å	88.2 °	Piskunov, A. V.; Lado, A. V.; Fukin, G. K.; Baranov, E. V.; Abakumova, L. G.; Cherkasov, V. K.; Abakumov, G. A. <i>Heteroat. Chem.</i> <b>2006</b> , <i>17</i> , 481-490.

4	CIXSUY	2.279 Å	87.1 °	Ramaswamy, P.; Datta, A.; Natarajan, S. <i>Eur. J. Inorg. Chem.</i> <b>2008</b> , 1376-1385.
4	TINOXL	2.311 Å	86.9 °	Christie, A. D.; Howie, R.A.; Moser, W. <i>Inorg. Chim. Acta</i> <b>1979</b> , 36, L447-L448.
	<b>Average:</b>	<b>2.233 Å</b>	<b>90.7 °/15 structures</b>	

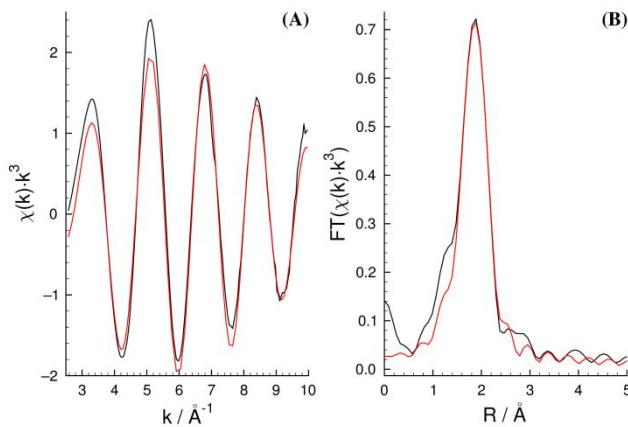
<i>N</i>	CSD code	$d_{\text{Sn-O}}$	Reference
5	KAKBEF	2.380 Å	Zabula, A. V.; Filatov, A. S.; Petrukhina, M. A. <i>J. Cluster Sci.</i> <b>2010</b> , 21, 361-370.
5	KAKBEF	2.380 Å	Zabula, A. V.; Filatov, A. S.; Petrukhina, M. A. <i>J. Cluster Sci.</i> <b>2010</b> , 21, 361-370.
5	KAKBEF	2.383 Å	Zabula, A. V.; Filatov, A. S.; Petrukhina, M. A. <i>J. Cluster Sci.</i> <b>2010</b> , 21, 361-370.
5	KAKBEF	2.383 Å	Zabula, A. V.; Filatov, A. S.; Petrukhina, M. A. <i>J. Cluster Sci.</i> <b>2010</b> , 21, 361-370.
5	OFACSO	2.392 Å	Birchall, T.; Johnson, J. P. <i>J. Chem. Soc., Dalton Trans.</i> <b>1981</b> , 69-73.
	<b>Average:</b>	<b>2.384 Å/5 structures</b>	

<i>N</i>	CSD code	$d_{\text{Sn-O}}$	Reference
6	CIXTIN	2.394 Å	Ramaswamy, P.; Datta, A.; Natarajan, S. <i>Eur. J. Inorg. Chem.</i> <b>2008</b> , 1376-1385.
6	SIHQEF	2.415 Å	Ayyappan, S.; Cheetham, A. K.; Natarajan, S.; Rao , C. N. R. <i>Chem. Mater.</i> <b>1998</b> , 10, 3746-3755.
6	XEXSAU	2.423 Å	Natarajan, S.; Vaidhyanathan, R.; Rao, C. N. R.; Ayyappan, S.; Cheetham, A. K. <i>Chem. Mater.</i> <b>1999</b> , 11, 1633-1639.
6	XEXRUN	2.424 Å	Natarajan, S.; Vaidhyanathan, R.; Rao, C. N. R.; Ayyappan, S.; Cheetham, A. K. <i>Chem. Mater.</i> <b>1999</b> , 11, 1633-1639.
6	NTBZSN10	2.441 Å	Ewings, P. F. R.; Harrison, P. G.; Morris, A.; King, T. J. <i>J. Chem. Soc., Dalton Trans.</i> , <b>1976</b> , 1602-1608.
6	FOTDEX	2.481 Å	Holt, E. M.; Klaui, W.; Zuckerman, J. J. <i>J. Organomet. Chem.</i> <b>1987</b> , 335, 29-42.
6	HATCIQ	2.498 Å	Macdonald, C. L. B.; Bandyopadhyay, R.; Cooper, B. F. T.; Friedl, W. W.; Rossini, A. J.; Schurko, R. W.; Eichhorn, S. H.; Herber, R. H. <i>J. Am. Chem. Soc.</i> <b>2012</b> , 134, 4332-4345.
6	HATCOW	2.523 Å	Macdonald, C. L. B.; Bandyopadhyay, R.; Cooper, B. F. T.; Friedl, W. W.; Rossini, A. J.; Schurko, R. W.; Eichhorn, S. H.; Herber, R. H. <i>J. Am. Chem. Soc.</i> <b>2012</b> , 134, 4332-4345.
	<b>Average:</b>	<b>2.450 Å/8 structures</b>	

<i>N</i>	CSD code	$d_{\text{Sn-O}}$	Reference
8	VUTHUO	2.597 Å	Bandyopadhyay, R.; Cooper, B. F. T.; Rossini, A. J.; Schurko, R. W.; Macdonald, C. L. B. <i>J. Organomet. Chem.</i> <b>2010</b> , 695, 1012-1018.
<b>Average:</b>		<b>2.597 Å/1 structure</b>	



**Figure S1.** Integrated Raman band intensities for the mode at  $\sim 430 \text{ cm}^{-1}$ , after background subtraction and deconvolution, as a function of the  $C_{\text{Sn(II)}}$ .



**Figure S2.** The experimental EXAFS spectrum of the Sn K-edge X-ray absorption spectra of  $0.1 \text{ mol}\cdot\text{dm}^{-3} \text{ SnCl}_2$  in  $1 \text{ mol}\cdot\text{dm}^{-3}$  hydrochloric acid (black) and the fitted spectrum (red) (A) and the Fourier-transform of the  $k^3$ -weighted EXAFS data of it and the fitted data (B).