Electronic Supplementary Material (ESI) for Dalton Transactions.

On solvated tin(IV) ions and the coordination chemistry of high-valent d^{10} metal ions

Daniel Lundberg* and Ingmar Persson

Electronic Supplementary Information

Table S1. Summary of bond distances in stannate(IV) and tin(IV) oxide compounds with the composition *i)* $[Sn(OH)_6^{2-}]$, *ii)* $(SnO_3^{2-})_n$ and $(SnO_4^{4-})_n$, *iii)* tin(IV) oxides, and *iv)* tin(IV) complexes with organic oxygen donor ligands. Red-marked references are considered outliers (including those with deviating chemical composition, and/or erroneous or incorrectly determined structures), and have not been included in the mean values. In addition, temperature/pressure modification measurements often yield multiple structure refcodes, where only one representative structure has been chosen to not skew mean values. Refcode given in numbers (ICSD; ref. 2) and letters (CSD; ref. 3).

***i)* $[Sn(OH)_6]^{2-}$**

Ref. code		
5120	1.973 Å	C. R. Ross, L. R. Bernstein and G. A. Waychunas, *Am. Mineralog.* 1988, **73**, 657-661. $(Mn_{0.94}/Fe_{0.06})[Sn_{0.98}/Si_{0.01}/Al_{0.01}(OH)_6]$
27147	1.976 Å	C. O. Bjoerling, *Am. J. Sci. Ser. 5* 1928, **15**, 297-302. $K_2[Sn(OH)_6]$.
27767	2.003 Å	C. Cohen-Addad, *Bull. Soc. Fr. Mineral. Cristall.* 1968, **91**, 315-324. $Zn[Sn(OH)_6]$.
25822	2.027 Å	H. Strunz and B. Contag, *Acta Crystallogr.* 1960, **13**, 601-603. $Mn[Sn(OH)_6]$.
25821	2.029 Å	H. Strunz and B. Contag, *Acta Crystallogr.* 1960, **13**, 601-603. $Fe[Sn(OH)_6]$.
25823	2.032 Å	H. Strunz and B. Contag, *Acta Crystallogr.* 1960, **13**, 601-603. $Co[Sn(OH)_6]$.
25825	2.032 Å	H. Strunz and B. Contag, *Acta Crystallogr.* 1960, **13**, 601-603. $Ca[Sn(OH)_6]$.
27146	2.032 Å	H. Strunz and B. Contag, *Acta Crystallogr.* 1960, **13**, 601-603. $Na_2[Sn(OH)_6]$.
25824	2.033 Å	H. Strunz and B. Contag, *Acta Crystallogr.* 1960, **13**, 601-603. $Mg[Sn(OH)_6]$.
YORJOG	2.043 Å	Y. Zhiliang R. Mockel, J. Bergunde and S. Dehnen, *Chem.-Eur. J.* 2014, **20**, 13491-13496. $[C_{54}H_{75}Cl_6Fe_3N_6O_6Sn_4][C_6H_5O_3Se]\cdot 4CHCl_3$. *$[Sn(\mu\text{-}OH)_6]$-moeity in larger framework.*
YORJIA	2.044 Å	Y. Zhiliang, R. Mockel, J. Bergunde and S. Dehnen, *Chem.-Eur. J.* 2014, **20**, 13491-13496. $[C_{54}H_{75}Cl_6Fe_3N_6O_6Sn_4][SnCl_3]\cdot CHCl_3\cdot \frac{1}{2}C_2Cl_4$. *$[Sn(\mu\text{-}OH)_6]$-moeity in larger framework.*
MAHQAP	2.045 Å	L. Plasseraud, H. Cattey and P. Richard, *Z.Naturforsch.,B:Chem.Sci.* 2010, **65**, 1293-1300. $[C_{72}H_{96}F_6O_{32}S_2Sn_{11}][CF_3O_3S]_6\cdot 2CH_2Cl_2$. *$[Sn(\mu\text{-}OH)_6]$-moeity in larger framework.*
27764	2.048 Å	C. Cohen-Addad, *Bull. Soc. Fr. Mineral. Cristall.* 1968, **91**, 315-324. $Ca[Sn(OH)_6]$.
280588	2.052 Å	S.-F. Yang, P. Y. Zavalii and M. S. Whittingham, *Acta Crystallogr., Sect. C* 2001, **57**, 228-229. $Li_2[Sn(OH)_6]$.
420543	2.055 Å	S. Kamaha and H. Reuter, *Z. Anorg. Allg. Chem.* 2009, **635**, 2058-2064. $Ba[Sn(OH)_6]\cdot 5H_2O$.
91102	2.059 Å	M.-M. Wu, X.-L. Li, G.-P. Shen, J. Li, R.-R. Xu and D. M. Proserpio, *J. Solid State Chem.* 2000, **151**, 56-60. $Sr_2[Sn(OH)_6](OH)_2$.
103	2.060 Å	E. Dubler, R. Hess and H. R. Oswald, *Z. Anorg. Allg. Chem.* 1976, **421**, 61-70. $[Cu(NH_3)_2][Sn(OH)_6]$.

85426	2.060 Å	H. Reuter and G. Bargon, *Z. Anorg. Allg. Chem.* 1997, **623**, 1978-1982. $Li_2[Sn(OH)_6]\cdot 2H_2O$.
92465	2.060 Å	H. Jacobs and R. Stahl, *Z. Anorg. Allgem. Chem.* 2000, **626**, 1863-1866. $Na_2[Sn(OH)_6]$
85487	2.061 Å	K. Nakata and H. Toyooka, *Osaka Kyoiku Daigaku Kiyo, Dai-3-bumon* 1997, **46**, 57-65. $Li_2[Sn(OH)_6]$.
188663	2.064 Å	S. Kamaha and H. Reuter, *Acta Crystallogr., Sect. E* 2013, **69**, i25-i25. $Li_2[Sn(OH)_6]\cdot 2H_2O$
94535	2.068 Å	S. I. Troyanov, A. V. Kostrikin, F. M. Spiridonov, I. V. Lin'ko, A. I. Ezhov, S. V. Martynova and B. E. Zaitsev, *Zh. Neorg. Khim.* 2001, **46**, 572-576. $K_2[Sn(OH)_6]$
92464	2.071 Å	H. Jacobs and R. Stahl, *Anorg. Allgem. Chem.* 2000, **626**, 1863-1866. $Na_2[Sn(OH)_6]$
194	2.091 Å	I. Morgenstern Badarau, *J Solid State Chem.* 1976, **17**, 399-406. $Cu[Sn(OH)_6]$.
15313	2.108 Å	A. N. Christensen and R. G. Hazell, *Acta Chem. Scand.* 1969, **23**, 1219-1224. $Mn[Sn(OH)_6]$.
85488	2.110 Å	K. Nakata and H. Toyooka, *Mem. Osaka Kyoiku Univ. Ser. III Nat. Sci. Appl. Sci.* 1997, **46**, 57-65. $Li_2[Sn(OH)_6]$.
76927	2.171 Å	L. C. Basciano, R. T. Peterson, P. L. Roeder and I. Swainson, *Can. Mineral.* 1998, **36**, 1203-1210. $Mg[Sn(OH)_6]$.
76928	2.181 Å	L. C. Basciano, R. T. Peterson, P. L. Roeder and I. Swainson, *Can. Mineral.* 1998, **36**, 1203-1210. $Mn[Sn(OH)_6]$.
Mean	**2.049 Å/20 structures**	

***ii*$_3$) $[SnO_3]^{2-}$**

Chain structures, six-coordinated

56095	1.960 Å	J. L. Hodeau, M. Marezio, A. Santoro and R. S. Roth, *J. Solid State Chem.* 1982, **45**, 170-179. $CaSnO_3$
27047	2.013 Å	H. D. Megaw, *Proc. Phys. Soc., London* 1946, **58**, 133-152. $SrSnO_3$
261491	2.032 Å	E. Moreira, J. M. Henriques, D. L. Azevedo, E. W. S. Caetano, V. N. Freire and E. L. Albuquerque, *J. Solid State Chem.* 2011, **174**, 921-928. $SrSnO_3$
2373	2.039 Å	B. Durand and H. Loiseleur, *J. Appl. Crystallog.* 1978, **11**, 289-290. $CaSnO_3$
29204	2.039 Å	B. Durand, M. Diot and P. Mollard, *Ann. Chim. (Paris)* 1979, **4**, 559-607. $CaSnO_3$
97432	2.039 Å	P. Schmid-Beurmann, V. Thangadurai and W. Weppner, *J. Solid State Chem.* 2003, **174**, 392-402. $SrSnO_3$
90846	2.049 Å	M. A. Green, K. Prassides, P. Day and D.A. Neumann, *Int. J. Inorg. Mater.* 2000, **2**, 35-41. $SrSnO_3$
153530*	2.050 Å	M. Glerup, K. S. Knight and F. W. Poulsen, *Mater. Res. Bull.* 2005, **40**, 507-520. $SrSnO_3$
90845	2.051 Å	M. A. Green, K. Prassides, P. Day and D.A. Neumann, *Int. J. Inorg. Mater.* 2000, **2**, 35-41. $SrSnO_3$
245943	2.051 Å	Y. Inaguma, M. Yoshida and T. Katsumata, *J. Am. Chem. Soc.* 2008, **130**, 6704-6705. $ZnSnO_3$
27049	2.054 Å	H. D. Megaw, *Proc. Phys. Soc., London* 1946, **58**, 133-152. $BaSnO_3$

180138	2.055 Å	A. S. Deepa, S. Vidya, P. C. Manu, S. Solomon, A. John and J. K. Thomas, *J. Alloys Compd.* 2011, **509**, 1830-1835. $BaSnO_3$
151591*	2.056 Å	J. Zhao, N. L. Ross and R. J. Angel, *Phys. Chem. Minerals* 2004, **31**, 299-305. $CaSnO_3$
161783	2.057 Å	S. Aleksovska, S. Dimitrovska and I. Kuzmanovski, *Acta Chim. Slov.* 2007, **54**, 574-582. $SrSnO_3$
165167	2.057 Å	H. Mizoguchi, H. W. Eng and P. M. Woodward, *Inorg. Chem.* 2004, **43**, 1667-1680. $CdSnO_3$
59161	2.060 Å	M. Vallet Regi, J. M. Gonzalez Calbet, M. A. Alario-Franco and A. Vegas, *Acta Crystallogr., Sect. C* 1986, **42**, 167-172. $SrSnO_3$
59160	2.061 Å	M. Vallet Regi, J. M. Gonzalez Calbet, M. A. Alario-Franco and A. Vegas, *Acta Crystallogr., Sect. C* 1986, **42**, 167-172. $CaSnO_3$
43138	2.062 Å	Y. Hinatsu, *J. Solid State Chem.* 1996, **122**, 384-389. $BaSnO_3$
260029	2.062 Å	M. Yoshida, T. Katsumata and Y. Inaguma, Y. *Inorg. Chem.* 2008, **47**, 6296-6302 $HgSnO_3$
21053	2.064 Å	G. Lang, *Z. Anorg. Allg. Chem.* 1966, **348**, 246-256. Li_2SnO_3
261492	2.064 Å	E. Moreira, J. M. Henriques, D. L. Azevedo, E. W. S. Caetano, V. N. Freire and E. L. Albuquerque, *J. Solid State Chem.* 2011, **174**, 921-928. $SrSnO_3$
21032	2.072 Å	G. Kreuzburg, F. Stewner and R. Hoppe, *Z. Anorg. Allg. Chem.* 1970, **379**, 242-254. Li_2SnO_3
89838	2.074 Å	T. Oku, A. Carlsson, J.-O. Bovin, C. Svensson, L. R. Wallenberg, C. Linke, and M. Jansen, *Acta Crystallogr., Sect. B* 2000, **56**, 363-368. Ag_2SnO_3
407237	2.074 Å	M. Jansen and C. Linke, *Anorg. Allg. Chem.* 1997, **623**, 1441-1446. Ag_2SnO_3
180402*	2.075 Å	P. D. Sesion, Jr., J. M. Henriques, C. A. Barboza, E. L. Albuquerque, V. N. Freire and E. W. S. Caetano, *J. Phys.: Condensed Matter* 2010, **22**, 435801-1-435801-13. $CdSnO_3$
50404	2.085 Å	D. Kovacheva and K. Petrov, *Solid State Ionics* 1998, **109**, 327-332. $ZnSnO_3$
29203	2.088 Å	B. Durand, M. Diot and P. Mollard, *Ann. Chim. (Paris)* 1979, **4**, 559-607. $MnSnO_3$
165122	2.105 Å	W. Hai, H. Haitao and W. Biao *Solid State Commun.* 2009, **149**, 1849-1852. $ZnSnO_3$
6325	2.111 Å	A. Verbaere, M. Dion and M. Tournoux, *J. Solid State Chem.* 1974, **11**, 184-189. Tl_2SnO_3
24561	2.149 Å	J. Zhao, N. L. Ross, R. J. Angel, *Phys. Chem. Miner.*, 2004, **31**, 299-305. $CaSnO_3$
Mean	**2.056 Å/23 structures**	

***** = representative structure of multiple temperature/pressure modifications

***ii*$_4$) $[SnO_4]^{4-}$**

Isolated four-coordinated

65970	1.955 Å	K. Bernet and R. Hoppe, *Z. Anorg. Allg. Chem.* 1990, **587**, 145-156. Cs_4SnO_4

202818	1.955 Å	K. Bernet and R. Hoppe, *Eur. J. Solid State Inorg. Chem.* 1988, **25**, 119-134. Na_4SnO_4
158	1.956 Å	R. Marchand, Y. Piffard and M. Tournoux, *Acta Crystallogr., Sect. B* 1975, **31**, 511-514. $K_4[SnO_4]$
280293	1.958 Å	C. Hoch and C. Roehr, *Acta Crystallogr., Sect. C* 2000, **56**, 136-137. Rb_4SnO_4
40217	1.959 Å	K. Bernet and R. Hoppe, *Z. Anorg. Allg. Chem.* 1989, **571**, 101-112. $RbNa_3SnO_4$
Mean	**1.957 Å/5 structures**	

Mixed four- and six-coordinated

24123	1.976 + 2.102 Å	P. Poix, *Ann. Chim. (Paris)* 1964, 261-285. $CoMgSnO_4$
28239	2.153 + 2.095 Å	J. Choisnet, A. Deschanvres and B. Raveau, *Comptes Rendus Hebdomadaires des Seances de l'Academie des Sciences*, *Serie C, Sciences Chimiques* 1968, **266**, 543-545. $(Zn_{1.2}Cd_{0.8})SnO_4$

Chain structures, six-coordinated

9010	2.029 Å	M. Troemel, *Z. Anorg. Allg. Chem.* 1969, **371**, 237-247. Cd_2SnO_4
24234	2.032 Å	T. F. W. Barth and E. Posnjak, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* 1932, **82**, 325-341. Zn_2SnO_4
84245	2.034 Å	B. J. Kennedy, *Aust. J. Chem.* 1997, **50**, 917-919. Sr_2SnO_4
81852	2.037 Å	M. A. Green, K. Prassides, P. Day and J. K. Stalick, *J. Chem. Soc., Faraday Trans.* 1996, **92**, 2155-2159. Sr_2SnO_4
81851	2.039 Å	M. A. Green, K. Prassides, P. Day and J. K. Stalick, *J. Chem. Soc., Faraday Trans.* 1996, **92**, 2155-2159. Sr_2SnO_4
28235	2.041 Å	J. Choisnet, A. Deschanvres and B. Raveau, *Comptes Rendus Hebdomadaires des Seances de l'Academie des Sciences*, *Serie C, Sciences Chimiques* 1968, **266**, 543-545. Zn_2SnO_4
150385*	2.041 Å	W. T. Fu, D. Visser, K. S. Knight and D. J. W. Ijdo, *J. Solid State Chem.* 2004, **177**, 4081-4086. Sr_2SnO_4
59760*	2.043 Å	W. T. Fu, D. Visser and D. J. W. Ijdo, *J. Solid State Chem.* 2002, **169**, 208-213. Sr_2SnO_4
35728	2.049 Å	P. Lacorre, M. Hervieu, J. Pannetier, J. Choisnet and B. Raveau, *J. Solid State Chem.* 1983, **50**, 196-203. $LiFeSnO_4$
35726	2.052 Å	P. Lacorre, M. Hervieu, J. Pannetier, J. Choisnet and B. Raveau, *J. Solid State Chem.* 1983, **50**, 196-203. $LiFeSnO_4$
27115	2.062 Å	R. Weiss and R. Faivre, *Comptes Rendus Hebdomadaires des Seances de l'Academie des Sciences* 1959, **248**, 106-108. Ba_2SnO_4
84246	2.065 Å	B. J. Kennedy, *Aust. J. Chem.* 1997, **50**, 917-919. Ba_2SnO_4
81849	2.066 Å	M. A. Green, K. Prassides, P. Day and J. K. Stalick, *J. Chem. Soc., Faraday Trans.* 1996, **92**, 2155-2159. Ba_2SnO_4
81850	2.069 Å	M. A. Green, K. Prassides, P. Day and J. K. Stalick, *J. Chem. Soc., Faraday Trans.* 1996, **92**, 2155-2159. Ba_2SnO_4
69297	2.069 Å	M. E. Bowden and C. M. Cardile, *Powder Diffraction* 1990, **5**, 36-40. Cd_2SnO_4

28199	2.076 Å	V. A. Bokov, G. V. Novikov, O. B. Proskuryakov, Y. G. Saksonov, V. A. Trukhtanov and S. I. Yushchuk, *Fizika Tverdogo Tela (Leningrad)* 1968, **10**, 1080-1084. Mg_2SnO_4
24127	2.077 Å	P. Poix, *Ann. Chim. (Paris)* 1964, 261-285. Mg_2SnO_4
69296	2.088 Å	M. E. Bowden and C. M. Cardile, *Powder Diffraction* 1990, **5**, 36-40. Cd_2SnO_4
187742	2.094 Å	T. Ishigaki, A. Torisaka, K. Nomizu, P. Madhusudan, K. Uematsu, K. Toda and M. Sato, *Dalton Trans.* 2013, **42**, 4781-4785. Ca_2SnO_4
193154	2.095 Å	K. Jeyadheepan and C. Sanjeeviraja, *J. Chem.* 2014, **7**, 245918/1-6. Zn_2SnO_4.
173626	2.098 Å	H. Yamane, Y. Kaminaga, S. Abe and T. Yamada, *J. Solid State Chem.* 2008, **181**, 2559-2564. Ca_2SnO_4
9011	2.101 Å	M. Troemel, *Z. Anorg. Allg. Chem.* 1969, **371**, 237-247. Ca_2SnO_4
28491	2.151 Å	M. Nogues and P. Poix, *Ann. Chim. (Paris)* 1968, 335-345. Mn_2SnO_4
69299	2.241 Å	M. E. Bowden and C. M. Cardile, *Powder Diffraction* 1990, **5**, 36-40. Cd_2SnO_4
69298	2.244 Å	M. E. Bowden and C. M. Cardile, *Powder Diffraction* 1990, **5**, 36-40. Cd_2SnO_4
Mean	**2.060 Å/21 structures**	

***** = representative structure of multiple temperature/pressure modifications

Hexanitratotin(IV) complex

EXEHAS	2.072 Å	P. Portius, B. Peerless, M. Davis and R. Campbell, *Inorg.Chem.* 2016, **55**, 8976-8984. $2[(C_6H_5)_3PNP(C_6H_5)_3][Sn(NO_3)_6]\cdot 2\,CH_3CN$

***iii)* SnO_2**

169032	2.033 Å	A. Gupta, A. Kumar, M. S. Hegde and U. V. Waghmare, *J. Chem. Phys.* 2010, **132**, 194702-1-194702-8.
181276	2.038 Å	Z. Bo, L. C. Mei, L. M. Bang, C. X. Rong, Z. Jun, J. G. Fu, *Phys. B: Condensed Matter* 2011, **406**, 3508-3513.
157449	2.048 Å	L. Gracia, A. Beltran and J. Andres, *J. Phys. Chem. B* 2007, **111**, 6479-6485.
90611	2.050 Å	M. Klementova, M. Rieder and Z. Weiss, *Int. J. Inorg. Mater.* 2000, **45**, 155-157.
157448	2.050 Å	L. Gracia, A. Beltran and J. Andres, *J. Phys. Chem. B* 2007, **111**, 6479-6485.
169033	2.050 Å	A. Gupta, A. Kumar, M. S. Hegde and U. V. Waghmare, *J. Chem. Phys.* 2010, **132**, 194702-1-194702-8.
154960	2.051 Å	B. Grzeta, E. Tkalcec, C. Goebbert, M. Takeda, M. Takahashi, K. Nomura and M. Jaksic, *J. Phys. Chem. Solids* 2002, **63**, 765-772.

56671	2.053 Å	J. Haines and J. M. Leger, *Phys. Rev. B* 1997, **55**, 11144-11154
16635	2.053 Å	W. H. Baur, *Acta Crystallogr.* 1956, **9**, 515-520.
160667	2.053 Å	T. Maekawa, C. Minagoshi, S. Nakamura, K. Nomura and H. Kageyama, *Chem. Sensors, Jpn.* 2008, **24**, 19-21
9163	2.054 Å	W. H. Baur and A. A. Khan, *Acta Crystallogr., Sect. B* 1971, **27**, 2133-2139.
39173	2.054 Å	H. Seki, N. Ishizawa, N. Mizutani and M. Kato, *J. Ceram. Assoc. Jpn.* 1984, **92**, 219-223; *Powder Diffraction* 1989, **4**, 156-160.
647469	2.054 Å	Z. Bo, L. C. Mei, L. M. Bang, C. X. Rong, Z. Jun, J. G. Fu, *Phys. B: Condensed Matter* 2011, **406**, 3508-3513.
84576	2.055 Å	A. A. Bolzan, C. Fong, B. J. Kennedy and C. J. Howard, *Acta Crystallogr., Sect. B* 1997, **53**, 373-380.
92552	2.055 Å	T. Yamanaka, R. Kurashima and J. Mimaki, *Z. Kristallogr.* 2000, **215**, 424-428.
91517	2.057 Å	Y.-I. Kim, M.-J. Jung and K. H. Kim, *Korean J. Ceram.* 2000, **6**, 354-358.
157450	2.058 Å	L. Gracia, A. Beltran and J. Andres, *J. Phys. Chem. B* 2007, **111**, 6479-6485.
157451	2.068 Å	L. Gracia, A. Beltran and J. Andres, *J. Phys. Chem. B* 2007, **111**, 6479-6485.
62199	2.092 Å	E. Müller, *Acta Crystallogr., Sect. B* 1984, 40, 359-363.
Mean	**2.052 Å/18 structures**	

***iv)* Tin(IV) complexes containing anionic organic ligands**

Four-coordinate structures

VISKIR	1.948 Å	M. J. Hampden-Smith, T. A. Wark, A. Rheingold and J. C. Huffman, *Can. J. Chem.* 1991, **69**, 121-129. $Sn(C_4H_9O)_4$

Five-coordinate structures

SIHNEC	2.011 Å	M. Veith and M. Reimers, *Chem. Ber.* 1990, **123**, 1941-1944. $(C_{40}H_{90}K_2O_{10}Sn_2)_n\ n(C_7H_8)$
EKOBEM	2.146 Å	B. Ruan, Y. Tian, H. Zhou, J. Wu, R. Hu, C. Zhu, J. Yang and H. Zhu *Inorg. Chim. Acta* 2011, **365**, 302-308.

Six-coordinate structures (selected, excluding those with Sn-O-Sn bonds)

RIZREX	2.019 Å	B. Jirjahn, H. Hildebrandt and G. Heller, *Z. Naturforsch., Teil B* 1997, **52**, 95-101.
DEPMET	2.030 Å	M. C. Barry, C. M. Lieberman, Z. Wei, R. Clerac, A. S. Filatov and E. V. Dikarev, *Inorg. Chem.* 2018, **57**, 2308-2313.
DEPMOD	2.031 Å	M. C. Barry, C. M. Lieberman, Z. Wei, R. Clerac, A. S. Filatov and E. V. Dikarev, *Inorg. Chem.* 2018, **57**, 2308-2313.
DEPMUJ	2.031 Å	M. C. Barry, C. M. Lieberman, Z. Wei, R. Clerac, A. S. Filatov and E. V. Dikarev, *Inorg. Chem.* 2018, **57**, 2308-2313.
YUNDAM	2.038 Å	I. Abrahams, M. Motevalli, S. A. A. Shah and A. C. Sullivan, *J. Organomet. Chem.* 1995, **492**, 99-104.

RAWWOC	2.043 Å	S. N. Brown, E. T. Chu, M. W. Hull and B. C. Noll, *J. Am. Chem. Soc.* 2005, **127**, 16010-16011.
IQIPED	2.044 Å	L. Jager, V. Lorenz, T. Muller, H.-P. Abicht, M. Rossel and H. Gorls, *Z. Anorg. Allg. Chem.* **2004**, *630*, 189-195.
VOHTIX	2.044 Å	G. A. Seisenbaeva, S. D. Topel and V. G. Kessler, *Polyhedron* **2014**, *81*, 21-26.
AFEXEQ	2.045 Å	E. E. Martsinko, I. K. Minacheva, E .A. Chebanenko, I. I. Seifullina, V. S. Sergienko and A. V. Churakov, *Zh. Neorg. Khim.* 2013, **58**, 588.
QAZDEA	2.046 Å	M. Verdenelli, S. Parola, L. G. Hubert-Pfalzgraf and S. Lecocq, *Polyhedron* 2000, **19**, 2069-2075.
AFEYAN	2.046 Å	E. E. Martsinko, I. K. Minacheva, E .A. Chebanenko, I. I. Seifullina, V. S. Sergienko and A. V. Churakov, *Russ. J. Inorg. Chem.* 2013, **58**, 515-522.
NIRYIX	2.052 Å	B. F. Abrahams, N. J. FitzGerald and R. Robson, *Angew. Chem., Int. Ed.* 2007, **46**, 8640-8643.
KIHCIN	2.053 Å	T. A. Wark, E. A. Gulliver, M. J. Hampden-Smith and A. L. Rheingold, *Inorg. Chem.* 1990, **29**, 4360-4362.
QIRPAI	2.054 Å	X. Sun, D. W. Johnson, D. L. Caulder, K. N. Raymond and E. H. Wong, *J.Am. Chem.Soc.* 2001, **123**, 2752-2763.
VOHTET	2.054 Å	G. A. Seisenbaeva, S. D. Topel and V. G. Kessler, *Polyhedron* 2014, **81**, 21-26.
LAGLEN	2.057 Å	M. B. Diop, L. Diop, L. Plasseraud and T. Maris, *Acta Crystallogr., Sect. E* 2016, **72**, 355-357.
QAWMIM	2.058 Å	P. C. Andrews, P. C. Junk, I. Nuzhnaya and D. T. Thielemann, *Inorg. Chem.* 2012, **51**, 751-753.
KOBXEF	2.059 Å	S.-L. Li, Y.-Q. Lan, J.-F. Ma, J. Yang, M. Zhang and Z.-M. Su *Inorg. Chem.* 2008, **47**, 2931-2933.
JIRJEA	2.059 Å	G. A. Abakumov, V. K. Cherkasov, A. V. Piskunov, A. V. Lado, G. K. Fukin and E. V. Baranov, *Dokl. Akad. Nauk SSSR* 2006, **410**, 145-149.
JELMOC	2.060 Å	M. J. Hampden-Smith, D. E. Smith and E. N. Duesler, *Inorg. Chem.* 1989, **28**, 3399-3401.
FESJES	2.060 Å	X. Sun, D. W. Johnson, D. L. Caulder, R. E. Powers, K. N. Raymond and E. H. Wong, *Angew. Chem., Int. Ed.* 1999, **38**, 1303-1307.
VOLMIS	2.061 Å	C. Lamberth, J. C. Machell, D. M. P. Mingos and T. L. Stolberg, *J. Mater. Chem.* 1991, **1**, 775-780.
KOBXIJ	2.062 Å	S.-L. Li, Y.-Q. Lan, J.-F. Ma, J. Yang, M. Zhang and Z.-M. Su, *Inorg. Chem.* 2008, **47**, 2931-2933.
GANYOJ	2.062 Å	T. A. Annan, R. K. Chadha, D. G. Tuck and K. D. Watson, *Can. J. Chem.* 1987, **65**, 2670-2676.
GAJFUS	2.063 Å	R. R. Holmes, S. Shafieezad, V. Chandrasekhar, A. C. Sau, J. M. Holmes and R. A. Day, *J. Am. Chem. Soc.* 1988, **110**, 1168-1174.
VERDUS	2.065 Å	K. Benner, J. Ihringer, P. Klufers and D. Marinov, *Angew. Chem., Int. Ed.* 2006, **45**, 5818-5822.
QAWMEI	2.069 Å	P. C. Andrews, P. C. Junk, I. Nuzhnaya and D. T. Thielemann, *Inorg. Chem.* 2012, **51**, 751-753.
NOWWEB	2.070 Å	P. R. Deacon, M. F. Mahon, K. C. Molloy and P. C. Waterfield, *J. Chem. Soc., Dalton Trans.* 1997, 3705-3712.

XEXSOJ	2.072 Å	A. V. Piskunov, A. V. Lado, G. K. Fukin, E. V. Baranov, L. G. Abakumova, V. K. Cherkasov and G. A. Abakumov, *Heteroat. Chem.* 2006, **17**, 481-490.
XEXSID	2.074 Å	A. V. Piskunov, A. V. Lado, G. K. Fukin, E. V. Baranov, L. G. Abakumova, V. K. Cherkasov and G. A. Abakumov, *Heteroat. Chem.* 2006, **17**, 481-490.

Mean Sn-O bond distance: 2.054 Å/30 structures

Six-coordinate structures (small binuclear, both tin(IV))

ZEBNEZ	2.043 Å	C. D. Chandler, J. Caruso, M. J. Hampden-Smith and A. L. Rheingold, *Polyhedron* 1995, **14**, 2491-2497.
VISKOX	2.050 Å	M. J. Hampden-Smith, T. A. Wark, A. L. Rheingold and J. C. Huffman, *Can. J. Chem.* 1991, **69**, 121-129.
VISKOX01	2.053 Å	H. Reuter and M. Kremser, *Z. Anorg. Allg. Chem.* 1991, **598**, 259-268.
TIRHAF	2.056 Å	C. Leonhardt, S. Brumm, A. Seifert, G. Cox, A. Lange, T. Ruffer, D. Schaarschmidt, H. Lang, N. Johrmann, M. Hietschold, F. Simon and M. Mehring, *ChemPlusChem* 2013, **78**, 1400-1412.
FICDIE	2.058 Å	C. D. Chandler, G. D. Fallon, A. J. Koplick and B. O. West, *Aust. J. Chem.* 1987, **40**, 1427-1439.
TIRGUY	2.076 Å	C. Leonhardt, S. Brumm, A. Seifert, G. Cox, A. Lange, T. Ruffer, D. Schaarschmidt, H. Lang, N. Johrmann, M. Hietschold, F. Simon and M. Mehring, *ChemPlusChem* 2013, **78**, 1400-1412.

Mean Sn-O bond distance: 2.056 Å/6 structures

Seven-coodinate structures

KSNOXT	2.115 Å	G. J. Kruger, E. L. .J. Breet and R. van Eldik, *Inorg. Chim. Acta* 1976, **19**, 151-157.
PACSNA	2.125 Å	N. W. Alcock and V. L. Tracy, *J. Chem. Soc., Dalton Trans.* 1976, 2246-2249.
ROPYEA	2.140 Å	M. C. Barret, M. F. Mahon, K. C. Molloy and P. Wright, *Main Group Met. Chem.* 2000, **23**, 663-672.
TRSNOH	2.121 Å	J. J. Park, D. M. Collins and J. L. Hoard, *J. Am. Chem. Soc.* 1970, **92**, 3636-3644.
VEDKAR	2.135 Å	E. Martinez-Ferrero, K. Boubekeur and F. Ribot, *Eur. J. Inorg. Chem.* 2006, 802-807. (binuclear)

5 structures – mean Sn-O bond distance: 2.127 Å

Eight-coodinate structures

HOKVIM	2.164 Å	L. Párkányi, A. Kálmán, A. Deák, M. Venter and I. Haiduc, *Inorg. Chem. Commun.* 1999, **2**, 265-268.
PUMCAB	2.169 Å	M. Kira, L. C. Zhang, C. Kabuto and H. Sakurai, *Organometallics* 1998, **17**, 887-892.

MULPUE	2.171 Å	L. Abis, D. B. Dell'Amico, F. Calderazzo, R. Caminiti, F. Garbassi, S. Ianelli, G. Pelizzi, P. Robino and A. Tomei, *J. Mol. Catal. A:Chem.* 1996, **108**, L113-L117.
BAKBEW	2.175 Å	B. F. Abrahams, M. J. Grannas, T. A. Hudson, S. A. Hughes, N. H. Pranoto and R. Robson, *Dalton Trans.* 2011, **40**, 12242-12247.
BAKBIA	2.175 Å	B. F. Abrahams, M. J. Grannas, T. A. Hudson, S. A. Hughes, N. H. Pranoto and R. Robson, *Dalton Trans.* 2011, **40**, 12242-12247.
HENJAO	2.177 Å	G. J.-P. Deblonde, T. D. Lohrey, D. D. An and R. J. Abergel, *New J. Chem.* 2018, **42**, 7649-7658.
BAKBOG	2.178 Å	B. F. Abrahams, M. J. Grannas, T. A. Hudson, S. A. Hughes, N. H. Pranoto and R. Robson, *Dalton Trans.* 2011, **40**, 12242-12247.
UGOZUL	2.181 Å	G. A. Horley, M. F. Mahon, K. C. Molloy, P. W. Haycock and C. P. Myers, *Inorg. Chem.* 2002, **41**, 5052-5058.
XIVBIP	2.184 Å	N. Gueye, L. Diop and H. Stoeckli-Evans, *Acta Crystallogr., Sect. E* 2014, **70**, m49-m50.
ACETSN01	2.218 Å	N. W. Alcock and V. L. Tracy, *Acta Crystallogr., Sect. B* 1979, **35**, 80-83.

9 structures – mean Sn-O bond distance: 2.175 Å

Nine-coodinate structures

None reported

Mean Sn-O bond distances (±s)

All four-coordinate tin(IV) complexes: 1.955(4) Å /6 structures

All five-coordinate tin(IV) complexes: 2.011 Å /1 structure

All six-coordinate tin(IV) complexes (and oxides): 2.053(13) Å /114 structures

All seven-coordinate tin(IV) complexes: 2.127(10) Å /5 structures

All eight-coordinate tin(IV) complexes: 2.175(6) Å /9 structures

Table S2. Summary of mean bond distances in six-coordinate tin(IV) compounds with S-donors. The given refcode refers to the respective structure's CSD entry, ref. 3. Mean bond distances are listed for all Sn-S bonds, but also shown separated into bonding type ($Sn\text{-}S_{\mu 2}$/$Sn\text{-}S_{\kappa}$).

Six-coordinate structures (small binuclear, both tin(IV))

	2.534 Å (2.463 Å/2.571 Å)	H. Reuter and M. Kremser, *Z. Anorg. Allg. Chem.* 1991, **598**, 259-268.
NOPTET	2.536 Å (2.469 Å/2.569 Å)	C. Leonhardt, S. Brumm, A. Seifert, G. Cox, A. Lange, T. Ruffer, D. Schaarschmidt, H. Lang, N. Johrmann, M. Hietschold, F. Simon and M. Mehring, *ChemPlusChem* 2013, **78**, 1400-1412.
KEFBUS	2.537 Å (2.448 Å/2.582 Å)	M. J. Hampden-Smith, T. A. Wark, A. L. Rheingold and J. C. Huffman, *Can. J. Chem.* 1991, **69**, 121-129.
YONXUW	2.539 Å (2.448 Å/2.585 Å)	C. D. Chandler, G. D. Fallon, A. J. Koplick and B. O. West, *Aust. J. Chem.* 1987, **40**, 1427-1439.
FADYOZ	2.542 Å (2.450 Å/2.588 Å)	C. D. Chandler, J. Caruso, M. J. Hampden-Smith and A. L. Rheingold, *Polyhedron* 1995, **14**, 2491-2497.

5 structures – mean Sn-S bond distance: 2.538(3) Å (2.456 Å/2.579 Å)

Table S3a. The .cif file for **1**, $[Sn(OS(CH_3)_2)_5CH_3](ClO_4)_3$. *Note:* The hkl part of the .cif file has been deleted from this table due to its length. It can be obtained for free upon request at the Cambridge Crystallographic Data Centre (CCDC) at <https://www.ccdc.cam.ac.uk/structures/>.

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 of a crystalline, structurally determined compound\
 [Sn(OS(CH3)2)5CH3](ClO4)3 whereas a similar reaction in\
 N,N-dimethylthioformamide (dmtf) forms a crystalline solid\
 with a binuclear [Sn2(SH)2(SCHN(CH3)2)8]6+ entity whose exact\
 formula remains undetermined. Both solids precipitate with\
 time in their respective mother liquids and constitute the\
 first two tin(IV) and even tetravalent d10 metal ion solvate\
 complexes reported. An EXAFS study showed that the structure\
 of the [Sn(OS(CH3)2)5CH3)]3+ complex is identical in solid\
 state and dimethylsulfoxide solution. While the exact\
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H6B H 0.632131 0.197850 0.688796 0.096 Uiso 1 1 calc R U . . .
H6C H 0.632872 0.299523 0.675741 0.096 Uiso 1 1 calc R U . . .
Cl1 Cl 0.24363(8) 0.51909(5) 0.85942(4) 0.0703(2) Uani 1 1 d D . . . .
O11 O 0.3005(3) 0.4704(2) 0.81195(19) 0.1335(12) Uani 1 1 d D . . . .
O12 O 0.1533(3) 0.5683(2) 0.81741(18) 0.1347(13) Uani 1 1 d D . . . .
O13 O 0.1971(3) 0.4620(2) 0.90588(15) 0.1139(10) Uani 1 1 d D . . . .
O14 O 0.3229(3) 0.5782(2) 0.90249(17) 0.1089(9) Uani 1 1 d D . . . .
Cl2 Cl 0.24543(9) -0.00531(5) 0.89096(5) 0.0739(2) Uani 1 1 d D U . . .
O21 O 0.2019(13) 0.0629(5) 0.8521(7) 0.190(6) Uani 0.627(13) 1 d D . P A 1
O22 O 0.1560(7) -0.0363(7) 0.9269(5) 0.157(4) Uani 0.627(13) 1 d D . P A 1
O23 O 0.2682(9) -0.0734(6) 0.8484(7) 0.191(6) Uani 0.627(13) 1 d D . P A 1
O24 O 0.3426(10) 0.0173(8) 0.9414(7) 0.208(6) Uani 0.627(13) 1 d D . P A 1
O21B O 0.213(2) 0.0459(13) 0.9428(10) 0.224(10) Uani 0.373(13) 1 d D U P A 2
O22B O 0.1993(16) 0.0258(17) 0.8236(9) 0.205(12) Uani 0.373(13) 1 d D U P A 2
O23B O 0.3600(10) 0.0061(18) 0.8941(9) 0.212(10) Uani 0.373(13) 1 d D U P A 2
O24B O 0.226(2) -0.0861(8) 0.9001(12) 0.236(12) Uani 0.373(13) 1 d D U P A 2
Cl3 Cl 0.20400(8) 0.24935(6) 0.59644(7) 0.0830(3) Uani 1 1 d D U . . .
O31 O 0.1506(15) 0.2010(14) 0.6410(10) 0.190(9) Uani 0.433(12) 1 d D U P B 1
O32 O 0.2291(18) 0.1924(8) 0.5473(9) 0.211(9) Uani 0.433(12) 1 d D U P B 1
O33 O 0.1266(12) 0.3133(8) 0.5726(14) 0.185(9) Uani 0.433(12) 1 d D U P B 1
O34 O 0.3017(12) 0.2895(9) 0.6309(12) 0.220(9) Uani 0.433(12) 1 d D U P B 1
O31B O 0.1612(8) 0.1676(5) 0.6138(6) 0.123(4) Uani 0.567(12) 1 d D U P B 2
O32B O 0.191(2) 0.3028(9) 0.6504(10) 0.280(10) Uani 0.567(12) 1 d D U P B 2
O33B O 0.1447(10) 0.2756(10) 0.5280(6) 0.184(7) Uani 0.567(12) 1 d D U P B 2
O34B O 0.3209(5) 0.2410(7) 0.5937(5) 0.126(4) Uani 0.567(12) 1 d D U P B 2

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S1 0.0526(4) 0.0749(5) 0.0450(4) -0.0013(3) 0.0167(3) -0.0060(3)
C11 0.090(3) 0.099(3) 0.121(3) 0.004(3) 0.052(2) -0.033(2)
C12 0.067(2) 0.097(3) 0.104(3) 0.009(2) 0.027(2) 0.016(2)
O2 0.0846(14) 0.0479(10) 0.0581(11) 0.0070(9) 0.0293(10) 0.0162(10)
S2 0.0725(5) 0.0506(4) 0.0535(4) 0.0057(3) 0.0171(3) 0.0114(3)
C21 0.091(3) 0.088(3) 0.128(3) 0.032(2) 0.031(2) 0.039(2)
C22 0.105(3) 0.075(2) 0.102(3) 0.012(2) 0.011(2) -0.016(2)
O3 0.0536(11) 0.0454(10) 0.0683(12) -0.0022(9) 0.0035(9) 0.0065(8)
S3 0.0575(4) 0.0456(4) 0.0691(4) -0.0028(3) 0.0067(3) 0.0047(3)
C31 0.118(3) 0.0562(19) 0.080(2) 0.0082(17) 0.008(2) 0.013(2)
C32 0.107(3) 0.077(2) 0.069(2) -0.0171(18) 0.0191(19) 0.004(2)
O4 0.0542(11) 0.0589(12) 0.0670(12) -0.0086(9) 0.0250(9) -0.0112(9)
S4 0.0607(5) 0.0731(5) 0.0882(6) -0.0187(4) 0.0362(4) -0.0136(4)
C41 0.099(3) 0.172(5) 0.072(2) 0.017(3) 0.037(2) 0.010(3)

C42 0.058(2) 0.088(3) 0.143(4) 0.009(2) 0.033(2) 0.0087(19)
O5 0.0479(10) 0.0625(11) 0.0405(9) -0.0051(8) 0.0083(8) 0.0017(8)
S5 0.0497(4) 0.0616(4) 0.0422(3) -0.0019(3) 0.0064(3) 0.0025(3)
C51 0.080(2) 0.089(2) 0.0413(15) 0.0072(15) 0.0080(15) -0.0035(18)
C52 0.071(2) 0.077(2) 0.071(2) -0.0025(17) 0.0037(16) -0.0183(17)
C6 0.071(2) 0.0672(18) 0.0500(16) -0.0048(14) -0.0005(14) -0.0120(15)
Cl1 0.0799(5) 0.0664(5) 0.0674(5) 0.0034(4) 0.0204(4) 0.0037(4)
O11 0.172(3) 0.120(3) 0.132(3) -0.016(2) 0.090(2) 0.009(2)
O12 0.127(3) 0.120(3) 0.139(3) 0.021(2) -0.025(2) 0.027(2)
O13 0.146(3) 0.113(2) 0.0918(19) 0.0105(17) 0.0453(18) -0.029(2)
O14 0.105(2) 0.097(2) 0.119(2) -0.0057(17) 0.0062(17) -0.0146(17)
Cl2 0.0887(6) 0.0592(5) 0.0755(5) 0.0050(4) 0.0195(5) -0.0030(4)
O21 0.271(13) 0.082(5) 0.205(12) 0.066(6) 0.011(9) 0.032(5)
O22 0.143(6) 0.162(9) 0.189(7) 0.068(7) 0.093(5) 0.030(5)
O23 0.205(9) 0.114(7) 0.277(14) -0.094(8) 0.111(9) -0.001(6)
O24 0.159(9) 0.233(10) 0.200(11) -0.038(10) -0.047(8) -0.031(8)
O21B 0.30(2) 0.206(17) 0.218(16) -0.070(13) 0.179(16) 0.000(16)
O22B 0.150(12) 0.34(3) 0.113(9) 0.126(14) -0.010(8) -0.067(16)
O23B 0.077(6) 0.40(3) 0.155(13) -0.067(16) 0.018(7) -0.032(10)
O24B 0.38(3) 0.068(7) 0.27(2) 0.067(10) 0.07(2) -0.023(12)
Cl3 0.0692(5) 0.0711(5) 0.1183(8) 0.0024(5) 0.0424(5) 0.0008(4)
O31 0.143(10) 0.30(2) 0.146(11) 0.089(13) 0.079(9) -0.031(13)
O32 0.30(2) 0.144(10) 0.224(15) -0.083(10) 0.151(15) -0.008(11)
O33 0.121(8) 0.091(7) 0.35(3) 0.049(12) 0.060(14) 0.041(6)
O34 0.115(10) 0.165(12) 0.36(3) -0.073(13) -0.020(11) -0.043(8)
O31B 0.090(5) 0.092(4) 0.171(9) 0.045(5) -0.021(5) -0.030(3)
O32B 0.42(3) 0.183(11) 0.304(15) -0.122(12) 0.256(18) -0.041(14)
O33B 0.126(7) 0.244(17) 0.174(9) 0.132(10) 0.010(6) 0.005(8)
O34B 0.063(3) 0.171(9) 0.156(7) 0.051(6) 0.050(4) -0.001(4)

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All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
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Sn1 O5 2.0925(19) . ?
Sn1 O4 2.098(2) . ?
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Sn1 O2 2.099(2) . ?
Sn1 O1 2.113(2) . ?
O1 S1 1.5464(19) . ?
S1 C12 1.755(4) . ?
S1 C11 1.756(4) . ?

C11 H11A 0.9600 . ?
C11 H11B 0.9600 . ?
C11 H11C 0.9600 . ?
C12 H12A 0.9600 . ?
C12 H12B 0.9600 . ?
C12 H12C 0.9600 . ?
O2 S2 1.535(2) . ?
S2 C22 1.752(4) . ?
S2 C21 1.760(4) . ?
C21 H21A 0.9600 . ?
C21 H21B 0.9600 . ?
C21 H21C 0.9600 . ?
C22 H22A 0.9600 . ?
C22 H22B 0.9600 . ?
C22 H22C 0.9600 . ?
O3 S3 1.543(2) . ?
S3 C32 1.752(3) . ?
S3 C31 1.760(3) . ?
C31 H31A 0.9600 . ?
C31 H31B 0.9600 . ?
C31 H31C 0.9600 . ?
C32 H32A 0.9600 . ?
C32 H32B 0.9600 . ?
C32 H32C 0.9600 . ?
O4 S4 1.541(2) . ?
S4 C42 1.759(4) . ?
S4 C41 1.768(4) . ?
C41 H41A 0.9600 . ?
C41 H41B 0.9600 . ?
C41 H41C 0.9600 . ?
C42 H42A 0.9600 . ?
C42 H42B 0.9600 . ?
C42 H42C 0.9600 . ?
O5 S5 1.555(2) . ?
S5 C52 1.767(3) . ?
S5 C51 1.769(3) . ?
C51 H51A 0.9600 . ?
C51 H51B 0.9600 . ?
C51 H51C 0.9600 . ?
C52 H52A 0.9600 . ?
C52 H52B 0.9600 . ?
C52 H52C 0.9600 . ?
C6 H6A 0.9600 . ?
C6 H6B 0.9600 . ?
C6 H6C 0.9600 . ?
Cl1 O13 1.397(3) . ?
Cl1 O12 1.399(3) . ?
Cl1 O11 1.402(3) . ?
Cl1 O14 1.420(3) . ?
Cl2 O24B 1.268(10) . ?
Cl2 O21 1.311(7) . ?
Cl2 O23B 1.324(12) . ?
Cl2 O21B 1.344(10) . ?
Cl2 O22B 1.351(12) . ?
Cl2 O23 1.357(6) . ?

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Cl2 O24 1.366(8) . ?
Cl2 O22 1.407(6) . ?
Cl3 O32B 1.319(8) . ?
Cl3 O32 1.327(8) . ?
Cl3 O34 1.337(10) . ?
Cl3 O31 1.337(11) . ?
Cl3 O33 1.340(10) . ?
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Cl3 O33B 1.385(8) . ?
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O3 Sn1 O4 88.33(8) . . ?
O5 Sn1 O4 82.48(8) . . ?
O3 Sn1 C6 93.66(11) . . ?
O5 Sn1 C6 175.17(10) . . ?
O4 Sn1 C6 98.90(11) . . ?
O3 Sn1 O2 169.09(7) . . ?
O5 Sn1 O2 88.44(8) . . ?
O4 Sn1 O2 85.67(8) . . ?
C6 Sn1 O2 96.27(11) . . ?
O3 Sn1 O1 94.74(8) . . ?
O5 Sn1 O1 78.85(7) . . ?
O4 Sn1 O1 160.42(8) . . ?
C6 Sn1 O1 100.19(11) . . ?
O2 Sn1 O1 87.98(8) . . ?
S1 O1 Sn1 126.63(11) . . ?
O1 S1 C12 104.39(16) . . ?
O1 S1 C11 101.13(16) . . ?
C12 S1 C11 100.6(2) . . ?
S1 C11 H11A 109.5 . . ?
S1 C11 H11B 109.5 . . ?
H11A C11 H11B 109.5 . . ?
S1 C11 H11C 109.5 . . ?
H11A C11 H11C 109.5 . . ?
H11B C11 H11C 109.5 . . ?
S1 C12 H12A 109.5 . . ?
S1 C12 H12B 109.5 . . ?
H12A C12 H12B 109.5 . . ?
S1 C12 H12C 109.5 . . ?
H12A C12 H12C 109.5 . . ?
H12B C12 H12C 109.5 . . ?
S2 O2 Sn1 128.74(11) . . ?
O2 S2 C22 104.80(16) . . ?
O2 S2 C21 101.85(16) . . ?
C22 S2 C21 99.7(2) . . ?
S2 C21 H21A 109.5 . . ?
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S2 C21 H21B 109.5 . . ?
H21A C21 H21B 109.5 . . ?
S2 C21 H21C 109.5 . . ?
H21A C21 H21C 109.5 . . ?
H21B C21 H21C 109.5 . . ?
S2 C22 H22A 109.5 . . ?
S2 C22 H22B 109.5 . . ?
H22A C22 H22B 109.5 . . ?
S2 C22 H22C 109.5 . . ?
H22A C22 H22C 109.5 . . ?
H22B C22 H22C 109.5 . . ?
S3 O3 Sn1 128.91(11) . . ?
O3 S3 C32 104.09(15) . . ?
O3 S3 C31 101.62(15) . . ?
C32 S3 C31 99.94(19) . . ?
S3 C31 H31A 109.5 . . ?
S3 C31 H31B 109.5 . . ?
H31A C31 H31B 109.5 . . ?
S3 C31 H31C 109.5 . . ?
H31A C31 H31C 109.5 . . ?
H31B C31 H31C 109.5 . . ?
S3 C32 H32A 109.5 . . ?
S3 C32 H32B 109.5 . . ?
H32A C32 H32B 109.5 . . ?
S3 C32 H32C 109.5 . . ?
H32A C32 H32C 109.5 . . ?
H32B C32 H32C 109.5 . . ?
S4 O4 Sn1 126.53(11) . . ?
O4 S4 C42 102.41(18) . . ?
O4 S4 C41 102.93(18) . . ?
C42 S4 C41 100.5(2) . . ?
S4 C41 H41A 109.5 . . ?
S4 C41 H41B 109.5 . . ?
H41A C41 H41B 109.5 . . ?
S4 C41 H41C 109.5 . . ?
H41A C41 H41C 109.5 . . ?
H41B C41 H41C 109.5 . . ?
S4 C42 H42A 109.5 . . ?
S4 C42 H42B 109.5 . . ?
H42A C42 H42B 109.5 . . ?
S4 C42 H42C 109.5 . . ?
H42A C42 H42C 109.5 . . ?
H42B C42 H42C 109.5 . . ?
S5 O5 Sn1 125.02(10) . . ?
O5 S5 C52 103.34(14) . . ?
O5 S5 C51 101.52(14) . . ?
C52 S5 C51 100.26(16) . . ?
S5 C51 H51A 109.5 . . ?
S5 C51 H51B 109.5 . . ?
H51A C51 H51B 109.5 . . ?
S5 C51 H51C 109.5 . . ?
H51A C51 H51C 109.5 . . ?
H51B C51 H51C 109.5 . . ?
S5 C52 H52A 109.5 . . ?
S5 C52 H52B 109.5 . . ?

H52A C52 H52B 109.5 . . ?
S5 C52 H52C 109.5 . . ?
H52A C52 H52C 109.5 . . ?
H52B C52 H52C 109.5 . . ?
Sn1 C6 H6A 109.5 . . ?
Sn1 C6 H6B 109.5 . . ?
H6A C6 H6B 109.5 . . ?
Sn1 C6 H6C 109.5 . . ?
H6A C6 H6C 109.5 . . ?
H6B C6 H6C 109.5 . . ?
O13 Cl1 O12 110.2(2) . . ?
O13 Cl1 O11 109.5(2) . . ?
O12 Cl1 O11 108.7(2) . . ?
O13 Cl1 O14 109.18(19) . . ?
O12 Cl1 O14 108.1(2) . . ?
O11 Cl1 O14 111.2(2) . . ?
O24B Cl2 O23B 108.8(16) . . ?
O24B Cl2 O21B 112.9(12) . . ?
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O24B Cl2 O22B 114.5(13) . . ?
O23B Cl2 O22B 102.5(11) . . ?
O21B Cl2 O22B 110.0(13) . . ?
O21 Cl2 O23 112.5(7) . . ?
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O23 Cl2 O24 111.7(8) . . ?
O21 Cl2 O22 106.6(7) . . ?
O23 Cl2 O22 104.8(5) . . ?
O24 Cl2 O22 109.9(7) . . ?
O32 Cl3 O34 110.9(11) . . ?
O32 Cl3 O31 104.3(10) . . ?
O34 Cl3 O31 113.6(13) . . ?
O32 Cl3 O33 117.7(12) . . ?
O34 Cl3 O33 106.1(10) . . ?
O31 Cl3 O33 104.4(12) . . ?
O32B Cl3 O34B 109.5(10) . . ?
O32B Cl3 O33B 114.3(10) . . ?
O34B Cl3 O33B 108.6(6) . . ?
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ZERR 4.00 0.0060 0.0079 0.0096 0.000 0.006 0.000
LATT 1
SYMM -x, y+1/2, -z+1/2

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omit    4   4   0
omit   -2   2   3
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DELU 0.01 0.02 cl3 o31 cl3 o32 cl3 o33 cl3 o34
DELU 0.01 0.02 cl3 o31b cl3 o32b cl3 o33b cl3 o34b
WGHT    0.036100    1.327700
FVAR       0.05551   1.35719   0.43267   0.62655
SN1   6    0.679449    0.272984    0.815745    11.00000    0.04208    0.04120 =
      0.04101   -0.00053    0.00925   -0.00118
O1    3    0.850954    0.314887    0.806806    11.00000    0.04578    0.06758 =
      0.04497   -0.00390    0.01393   -0.00979
S1    4    0.919814    0.290023    0.745515    11.00000    0.05260    0.07490 =
      0.04497   -0.00128    0.01666   -0.00603
C11   1    1.016655    0.379483    0.748787    11.00000    0.08960    0.09917 =
      0.12098    0.00389    0.05163   -0.03332
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H11A  2    0.972173    0.432179    0.735536    11.00000   -1.50000
H11B  2    1.069380    0.369857    0.714996    11.00000   -1.50000
H11C  2    1.061365    0.385329    0.797619    11.00000   -1.50000
AFIX   0
C12   1    1.017683    0.207529    0.784767    11.00000    0.06735    0.09678 =
      0.10431    0.00934    0.02666    0.01596
AFIX 137
H12A  2    1.059605    0.226965    0.831630    11.00000   -1.50000
H12B  2    1.072839    0.195255    0.753020    11.00000   -1.50000
H12C  2    0.974127    0.155254    0.791119    11.00000   -1.50000
AFIX   0
O2    3    0.747886    0.145714    0.835254    11.00000    0.08460    0.04791 =
      0.05808    0.00702    0.02932    0.01620
S2    4    0.750419    0.087365    0.903121    11.00000    0.07250    0.05064 =
      0.05347    0.00570    0.01707    0.01135
C21   1    0.882294    0.028289    0.905679    11.00000    0.09105    0.08787 =
      0.12829    0.03191    0.03094    0.03942
AFIX 137
H21A  2    0.884059    0.004271    0.857972    11.00000   -1.50000
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H21B  2    0.886373   -0.018519    0.940760    11.00000   -1.50000
H21C  2    0.948381    0.066892    0.919699    11.00000   -1.50000
AFIX   0
C22   1    0.647905    0.003968    0.873866    11.00000    0.10536    0.07481 =
     0.10200    0.01159    0.01110   -0.01589
AFIX 137
H22A  2    0.569493    0.027548    0.867620    11.00000   -1.50000
H22B  2    0.656649   -0.041933    0.909972    11.00000   -1.50000
H22C  2    0.661411   -0.019401    0.827979    11.00000   -1.50000
AFIX   0
O3    3    0.611239    0.399910    0.817767    11.00000    0.05355    0.04542 =
     0.06833   -0.00223    0.00352    0.00653
S3    4    0.674996    0.485113    0.847589    11.00000    0.05752    0.04561 =
     0.06914   -0.00275    0.00667    0.00469
C31   1    0.603424    0.563672    0.785317    11.00000    0.11811    0.05624 =
     0.08019    0.00822    0.00838    0.01336
AFIX 137
H31A  2    0.626257    0.555666    0.738435    11.00000   -1.50000
H31B  2    0.625399    0.621521    0.803380    11.00000   -1.50000
H31C  2    0.519565    0.556692    0.780159    11.00000   -1.50000
AFIX   0
C32   1    0.613687    0.510826    0.924860    11.00000    0.10665    0.07700 =
     0.06944   -0.01707    0.01905    0.00354
AFIX 137
H32A  2    0.529258    0.512062    0.911400    11.00000   -1.50000
H32B  2    0.641613    0.567321    0.943387    11.00000   -1.50000
H32C  2    0.636603    0.467182    0.962125    11.00000   -1.50000
AFIX   0
O4    3    0.537492    0.227951    0.862110    11.00000    0.05423    0.05889 =
     0.06696   -0.00856    0.02498   -0.01118
S4    4    0.482255    0.274756    0.921413    11.00000    0.06074    0.07312 =
     0.08817   -0.01868    0.03619   -0.01357
C41   1    0.501881    0.197783    0.994092    11.00000    0.09903    0.17193 =
     0.07177    0.01672    0.03744    0.00981
AFIX 137
H41A  2    0.470508    0.141978    0.975982    11.00000   -1.50000
H41B  2    0.461330    0.217786    1.031911    11.00000   -1.50000
H41C  2    0.584460    0.191797    1.013840    11.00000   -1.50000
AFIX   0
C42   1    0.330246    0.262980    0.887764    11.00000    0.05825    0.08841 =
     0.14296    0.00859    0.03318    0.00868
AFIX 137
H42A  2    0.309119    0.295465    0.842873    11.00000   -1.50000
H42B  2    0.286675    0.285015    0.923397    11.00000   -1.50000
H42C  2    0.311981    0.202035    0.878656    11.00000   -1.50000
AFIX   0
O5    3    0.749550    0.303654    0.925124    11.00000    0.04792    0.06255 =
     0.04046   -0.00511    0.00835    0.00172
S5    4    0.879200    0.286630    0.963424    11.00000    0.04974    0.06160 =
     0.04223   -0.00191    0.00641    0.00248
C51   1    0.861569    0.263501    1.054414    11.00000    0.07954    0.08917 =
     0.04128    0.00715    0.00802   -0.00348
AFIX 137
H51A  2    0.810018    0.306284    1.069843    11.00000   -1.50000
H51B  2    0.937018    0.265647    1.086450    11.00000   -1.50000
```

```
H51C  2    0.828104    0.206021    1.056317    11.00000   -1.50000
AFIX   0
C52   1    0.940177    0.393210    0.975161    11.00000    0.07057    0.07719 =
      0.07100   -0.00246    0.00367   -0.01833
AFIX 137
H52A  2    0.943112    0.418315    0.927987    11.00000   -1.50000
H52B  2    1.018518    0.389943    1.003553    11.00000   -1.50000
H52C  2    0.892035    0.429285    1.000322    11.00000   -1.50000
AFIX   0
C6    1    0.606851    0.253597    0.704509    11.00000    0.07123    0.06720 =
      0.05005   -0.00481   -0.00048   -0.01196
AFIX 137
H6A   2    0.522339    0.254548    0.698102    11.00000   -1.50000
H6B   2    0.632131    0.197850    0.688796    11.00000   -1.50000
H6C   2    0.632872    0.299523    0.675741    11.00000   -1.50000
AFIX   0
rem
rem perchlorates
rem
CL1   5    0.243627    0.519094    0.859419    11.00000    0.07995    0.06635 =
      0.06736    0.00338    0.02036    0.00366
O11   3    0.300527    0.470384    0.811949    11.00000    0.17208    0.12033 =
      0.13154   -0.01567    0.08961    0.00934
O12   3    0.153256    0.568317    0.817414    11.00000    0.12653    0.12018 =
      0.13880    0.02071   -0.02540    0.02736
O13   3    0.197079    0.462049    0.905884    11.00000    0.14637    0.11251 =
      0.09183    0.01046    0.04529   -0.02855
O14   3    0.322923    0.578214    0.902492    11.00000    0.10539    0.09700 =
      0.11886   -0.00571    0.00624   -0.01457

CL2   5    0.245435   -0.005313    0.890956    11.00000    0.08869    0.05916 =
      0.07547    0.00497    0.01946   -0.00295
part 1
O21   3    0.201901    0.062908    0.852083    41.00000    0.27140    0.08177 =
      0.20480    0.06639    0.01082    0.03220
O22   3    0.156021   -0.036251    0.926940    41.00000    0.14322    0.16220 =
      0.18920    0.06764    0.09276    0.02955
O23   3    0.268210   -0.073393    0.848402    41.00000    0.20538    0.11422 =
      0.27749   -0.09409    0.11068   -0.00146
O24   3    0.342574    0.017349    0.941404    41.00000    0.15936    0.23321 =
      0.19977   -0.03831   -0.04736   -0.03134
part 2
O21B  3    0.212850    0.045941    0.942824   -41.00000    0.29770    0.20591 =
      0.21779   -0.06973    0.17861    0.00000
O22B  3    0.199261    0.025837    0.823556   -41.00000    0.14985    0.33994 =
      0.11299    0.12605   -0.01045   -0.06678
O23B  3    0.360042    0.006128    0.894103   -41.00000    0.07693    0.40407 =
      0.15458   -0.06739    0.01814   -0.03180
O24B  3    0.225905   -0.086145    0.900065   -41.00000    0.37762    0.06789 =
      0.26538    0.06687    0.06719   -0.02290
part 0
CL3   5    0.204000    0.249352    0.596435    11.00000    0.06916    0.07108 =
      0.11831    0.00235    0.04237    0.00076
part 1
O31   3    0.150570    0.201031    0.641009    31.00000    0.14254    0.29978 =
```

```
      0.14643    0.08863    0.07854   -0.03075
O32   3    0.229084    0.192408    0.547312    31.00000    0.30265    0.14437 =
      0.22448   -0.08276    0.15088   -0.00831
O33   3    0.126596    0.313251    0.572642    31.00000    0.12087    0.09122 =
      0.34853    0.04942    0.05984    0.04105
O34   3    0.301704    0.289503    0.630859    31.00000    0.11496    0.16457 =
      0.35530   -0.07304   -0.01991   -0.04311
part 2
O31B  3    0.161220    0.167628    0.613788   -31.00000    0.09019    0.09249 =
      0.17078    0.04516   -0.02134   -0.03012
O32B  3    0.191266    0.302819    0.650450   -31.00000    0.42448    0.18347 =
      0.30446   -0.12187    0.25591   -0.04146
O33B  3    0.144740    0.275619    0.527989   -31.00000    0.12625    0.24431 =
      0.17449    0.13176    0.01038    0.00484
O34B  3    0.320870    0.240955    0.593658   -31.00000    0.06339    0.17099 =
      0.15638    0.05110    0.05022   -0.00141
part 0

HKLF 4 1 1 0 0 0 1 0 0 0 1


REM  Pb4dmso_0m in P2(1)/c
REM R1 =  0.0262 for    5183 Fo > 4sig(Fo)  and  0.0332 for all    6063 data
REM    420 parameters refined using     80 restraints

END

WGHT      0.0360      1.3265

REM Highest difference peak  0.400,  deepest hole -0.317,  1-sigma level  0.053
Q1    1   0.3275 -0.0531  0.9231  11.00000  0.05    0.40
Q2    1   0.1303  0.5289  0.8679  11.00000  0.05    0.37
Q3    1   0.3157  0.0614  0.8713  11.00000  0.05    0.35
Q4    1   0.1335  0.0203  0.8909  11.00000  0.05    0.33
Q5    1   0.7088  0.2172  0.8276  11.00000  0.05    0.30
Q6    1   0.4494  0.2955  0.8790  11.00000  0.05    0.29
Q7    1   0.2165  0.5206  0.7898  11.00000  0.05    0.27
Q8    1   0.2263 -0.0422  0.8186  11.00000  0.05    0.26
Q9    1   0.8572  0.2681  0.8129  11.00000  0.05    0.25
Q10   1   0.3333  0.4543  0.8637  11.00000  0.05    0.24
Q11   1   0.2914  0.0351  0.9694  11.00000  0.05    0.23
Q12   1   0.1535  0.2218  0.5175  11.00000  0.05    0.23
Q13   1   0.3830  0.0221  0.8994  11.00000  0.05    0.23
Q14   1   0.1735  0.0108  0.9602  11.00000  0.05    0.23
Q15   1   0.7763  0.2756  0.8151  11.00000  0.05    0.23
Q16   1   0.7035  0.0474  0.8959  11.00000  0.05    0.22
Q17   1   0.9007  0.3440  0.8160  11.00000  0.05    0.22
Q18   1   0.1306  0.2834  0.6352  11.00000  0.05    0.21
Q19   1   0.2564  0.2528  0.6918  11.00000  0.05    0.21
Q20   1   1.0686  0.2540  0.8240  11.00000  0.05    0.21
;
_shelx_res_checksum   74623
```

Table S3b. Basic crystallographic information for **2**.

Unit formula	$Sn_2(SH)_2(C_2H_7NS)_8$, 4 $CF_3SO_3^-$, 2 HS^- (approx.)
Crystal system	Triclinic
Space group	*P*-1 (№ 2)
a/Å	10.46(1)
b/Å	13.06 (1)
c/Å	16.52 (1)
α/°	98.51(2)
β/°	99.72(2)
γ/°	103.45(2)
V/Å^3	2121(3)
Z	2
D_c/g cm^{-1}	1.5 (est.)
μ/mm^{-1}	1.1 (est.)

Table S4. Summary of mean M-O bond distances in other six-coordinate, high-valent d^{10} ions (mononuclear, neutral solvates). The given refcode refers to the respective structure's CSD (letters; ref. 3) or ICSD (numbers; ref. 4.) entry.

a) Gallium(III)

Six-coordination

Water

NABZIA	1.946 Å	S. J. Dalgarno, M. J. Hardie and C. L. Raston, *Cryst. Growth Des.* 2004, **4**, 227-234. $[Ga(H_2O)_6]^{3+}$
260428	1.946 Å	A. D. Hendsbee, C. C. Pye and J. D. Masuda, *Acta Crystallogr., Sect. E* 2009, **65**, i65-i65. $[Ga(H_2O)_6]^{3+}$
MAQKEV	1.950 Å	O. A. Gerasko, E. A. Mainicheva, D. Y. Naumov, N. V. Kuratieva, M. N. Sokolov and V. P. Fedin, *Inorg. Chem.* 2005, **44**, 4133-4135. $[Ga(H_2O)_6]^{3+}$
REZKOJ01	1.950 Å	A. Pietraszko, K. Lukaszewicz and L. F. Kirpichnikova, *Pol. J. Chem.* 1995, **69**, 922-930 (ICSD #110542). $[Ga(H_2O)_6]^{3+}$
REZKOJ	1.951 Å	A. Pietraszko, K. Lukaszewicz and L. F. Kirpichnikova, *Pol. J. Chem.* 1995, **69**, 922-930 (ICSD #110541). $[Ga(H_2O)_6]^{3+}$
83654	1.969 Å	K. Panneerselvam, M. Soriano-Garcia, S. Holguin-Quinones and E. M. Holt, *Acta Crystallogr., Sect. C* 1996, **52**, 1605-1607. $[Ga(H_2O)_6]^{3+}$

Dimethylsulfoxide (dmso)

FALWAR01	1.962 Å	E. J Chan, B. G. Cox, J. M. Harrowfield, M. I. Ogden, B. W. Skelton and A. H. White, *Inorg. Chim. Acta* 2004, **357**, 2365-2373. $[Ga(dmso)_6]^{3+}$
FALWAR	1.964 Å	E. J Chan, B. G. Cox, J. M. Harrowfield, M. I. Ogden, B. W. Skelton and A. H. White, *Inorg. Chim. Acta* 2004, **357**, 2365-2373. $[Ga(dmso)_6]^{3+}$
VAMNIH	1.974 Å	A. Molla-Abbassi, M. Skripkin, M. Kritikos, I. Persson, J. Mink and M. Sandström, *Dalton Trans.* 2003, 1746-1753 (ICSD #414686). $[Ga(dmso)_6]^{3+}$

Dimethylformamide (dmf)

FEGSUG	1.960 Å	T. Duan and H. Schnockel, *Z. Anorg. Allg. Chem.* 2004, **630**, 2622-2626. $[Ga(dmf)_6]^{3+}$

Urea

PAPWIN 1.954 Å K. Sardar, M. Dan, B. Schwenzer and C. N. R. Rao, *J. Mater. Chem.* 2005, **15**, 2175-2177. $[Ga(urea)_6]^{3+}$

Mean six-coordinate Ga-O bond distance: **1.957(9) Å** (11 structures)

b) Indium(III)

Six-coordination

Water

UHORUG 2.082 Å M. K. Kamunde-Devonish, D. B. Fast, Z. L. Mensinger, J. T. Gatlin, L. N. Zakharov, M. R. Dolgos and D. W. Johnson, *Inorg. Chem.* 2015, ***54***, 3913-3920. [outer part-tetraaquadihydroxidoindium(III)]

OLURUI 2.110 Å Y.-Q. Tian, C.-X. Cai, X.-J. Yuan, Y.-Z. Li, T.-W. Wang and X.-Z. You, *Chem. Lett.* 2003, ***32***, 796-797. [partially occupied metal center, In:Fe 70:30]

417334 2.106 Å A. B. Ilyukhin and M. A. Malyarik, *Zh. Neorg. Khim.* 1999, **44**, 532-535. $[In(H_2O)_6]^{3+}$

429698 2.117 Å N.-D. Van, F. M. Kleeberg and T. Schleid, *Z. Anorg. Allg. Chem.* 2015, **641**, 2484-2489. $[In(H_2O)_6]^{3+}$

417333 2.124 Å A. B. Ilyukhin and M. A. Malyarik, *Zh. Neorg. Khim.* 1999, **44**, 532-535. $[In(H_2O)_6]^{3+}$

UHOROA 2.132 Å M. K. Kamunde-Devonish, D. B. Fast, Z. L. Mensinger, J. T. Gatlin, L. N. Zakharov, M. R. Dolgos and D. W. Johnson, *Inorg. Chem.* 2015, ***54***, 3913-3920. [outer part-tetraaquadihydroxidoindium(III)]

NONDUQ 2.139 Å Z. L. Mensinger, J. T. Gatlin, S. T. Meyers, L. N. Zakharov, D. A. Keszler and D. W. Johnson, *Angew. Chem., Int.Ed.* 2008, ***47***, 9484-9486. [outer part-tetraaquadihydroxidoindium(III)]

UHORIU 2.139 Å M. K. Kamunde-Devonish, D. B. Fast, Z. L. Mensinger, J. T. Gatlin, L. N. Zakharov, M. R. Dolgos and D. W. Johnson, *Inorg. Chem.* 2015, ***54***, 3913-3920. [outer part-tetraaquadihydroxidoindium(III)]

OLURUI01 2.141 Å Y.-Q. Tian, C.-X. Cai, X.-J. Yuan, Y.-Z. Li, T.-W. Wang and X.-Z. You, *Chem. Lett.* 2003, ***32***, 796-797. $[In(H_2O)_6]^{3+}$

GUMWIU 2.144 Å D. G. Samsonenko, M. N. Sokolov, A. V. Virovets, N. V. Pervukhina and V. P. Fedin, *Eur. J. Inorg. Chem.* 2001, 167-172. $[In(H_2O)_6]^{3+}$

Dimethylsulfoxide (dmso)/water

IMISEC 2.124 Å T. G. Cherkasova and I. P. Goryunova, *Zh. Neorg. Khim.* 2003, **48**, 611-615 (ICSD #98755). $[In(H_2O)_4(dmso)_2]^{3+}$

Dimethylsulfoxide (dmso)

KENRIE01	2.131 Å	T. G. Cherkasova and Z. S. Tatarinova, *Izv. Vyssh. Uchebn. Zaved.* 1997, **40**, 26. $[In(dmso)_6]^{3+}$
KENRIE	2.140 Å	J. M. Harrowfield, B. W. Skelton and A. H. White, *Aust. J. Chem.* 1990, **43**, 759-763. $[In(dmso)_6]^{3+}$
VAMNON	2.145 Å	A. Molla-Abbassi, M. Skripkin, M. Kritikos, I. Persson, J. Mink and M. Sandström, *Dalton Trans.* 2003, 1746-1753 (ICSD #414687). $[In(dmso)_6]^{3+}$

Mean six-coordinate In-O bond distance: **2.130(9) Å** (9 structures)

c) Thallium(III)

Six-coordination

Water

n/a	2.235 Å	J. Glaser and G. Johansson, *Acta Chem. Scand., Ser. A* 1981, **35**, 639-644. $[Tl(H_2O)_6]^{3+}$ [*note:* solution state LAXS measurement, as the crystal structure is reported as 2.170 Å for #31759 in ICSD, though given as 2.23(5) Å in this reference]

Dimethylsulfoxide (dmso)

n/a	2.221 Å	G. Ma, A. Molla-Abbassi, M. Kritikos, A. Ilyukhin, F. Jalilehvand, V. G. Kessler, M. Skripkin, M. Sandström, J. Glaser, J. Näslund, I. Persson, *Inorg. Chem.* 2001, **40**, 6432-6438. $[Tl(dmso)_6]^{3+}$ (solid state EXAFS data)
NERWAI01	2.224 Å	G. Ma, A. Molla-Abbassi, M. Kritikos, A. Ilyukhin, F. Jalilehvand, V. G. Kessler, M. Skripkin, M. Sandström, J. Glaser, J. Näslund, I. Persson, *Inorg. Chem.* 2001, **40**, 6432-6438. $[Tl(dmso)_6]^{3+}$
QUXRAD	2.224 Å	M. Ghadermazi and F. Manteghi, *Acta Crystallogr., Sect. E* 2010, **66**, m812-m812. $[Tl(dmso)_6]^{3+}$
NERWAI	2.240 Å	G. Ma, A. Molla-Abbassi, M. Kritikos, A. Ilyukhin, F. Jalilehvand, V. G. Kessler, M. Skripkin, M. Sandström, J. Glaser, J. Näslund, I. Persson, *Inorg. Chem.* 2001, **40**, 6432-6438. $[Tl(dmso)_6]^{3+}$

Mean six-coordinate Tl-O bond distance: **2.229(8) Å** (5 structures)

d) Germanium(IV)

no hydrates or solvates reported

e) Lead(IV)

no hydrates or solvates reported

Table S5. Summary of mean M-O bond distances in other six-coordinate, high-valent d^{10} ions (hydroxides). The given refcode refers to the respective structure's CSD (letters; ref. 3), ICSD (numbers; ref. 4.) or COD (*numbers in italics*; ref. 5) entry.

a) Gallium(III)

Four-coordination – tetrahydroxidogallate(III)

n/a	1.83 Å	T. Radnai, S. Bálint, I. Bakó, T. Megyes, T. Grósz, A. Pallagi, G. Peintler, I. Pálinko and P. Sipos, *Phys. Chem. Chem. Phys.* 2014, **16**, 4023-4032. $[Ga(OH)_4]^-$ [*note:* solution state measurement]
TEHPUS	1.955 Å	M. Albrecht, S. Dehn and R. Frohlich, *Angew. Chem., Int. Ed.* 2006, **45**, 2792-2794. (μ-hydroxido) $[Ga(OH)_4]^-$

Six-coordination - hexahydroxidogallate(III)

240927	1.966 Å	Z. L. Mensinger, L. N. Zakharov and D. W. Johnson, *Acta Crystallogr., Sect. E* 2008, **64**, pi8-pi9. $[Ga(OH)_6]^{3-}$ (μ-hydroxido)
XEJFAV	1.969 Å	S. Himeno, S. Murata and K. Eda, *Dalton Trans.* 2009, 6114-6119. $[Ga(OH)_6]^{3-}$
UHOREQ	1.970 Å	M. K. Kamunde-Devonish, D. B. Fast, Z. L. Mensinger, J. T. Gatlin, L. N. Zakharov, M. R. Dolgos and D. W. Johnson, *Inorg. Chem.* 2015, **54**, 3913-3920. $[Ga(OH)_6]^{3-}$ [inner part-hexahydroxidogallium(III)] (also UHOSAN and UHOSER)
NONDUQ	1.973 Å	Z. L. Mensinger, J. T. Gatlin, S. T. Meyers, L. N. Zakharov, D. A. Keszler and D. W. Johnson, *Angew. Chem., Int.Ed.* 2008, ***47***, 9484-9486. $[Ga(OH)_6]^{3-}$ (μ-hydroxido)
UHORIU	1.973 Å	M. K. Kamunde-Devonish, D. B. Fast, Z. L. Mensinger, J. T. Gatlin, L. N. Zakharov, M. R. Dolgos and D. W. Johnson, *Inorg. Chem.* 2015, **54**, 3913-3920. $[Ga(OH)_6]^{3-}$ [inner part-hexahydroxidogallium(III)] (also UHOROA and UHORUG)
PIVJIN	1.980 Å	F. Rominger, A. Müller and U. Thewalt, *Chem. Ber.* 1994, **127**, 797-804. $[Ga(OH)_6]^{3-}$ (μ-hydroxido)
51891	1.983 Å	I. Rousselot, C. Taviot-Gueho, F. Leroux, P. Leone, P. Palvadeau and J. P. Besse, *J. Solid State Chem.* 2002, **167**, 137-144. $[Ga(OH)_6]^{3-}$ (μ-hydroxido)
8103865	2.004 Å	M. Loeper, W. Gessner, M. Schneider and G. Reck, *Z. Kristallogr.* 1996, **211**, 709-710. $Na_9(Ga(OH)_6)_2(OH)_3 \cdot 6\ H_2O$
UHOREQ*	2.052 Å	M. K. Kamunde-Devonish, D. B. Fast, Z. L. Mensinger, J. T. Gatlin, L. N. Zakharov, M. R. Dolgos and D. W. Johnson, *Inorg. Chem.* 2015, **54**, 3913-3920. $[Ga(OH)_6]^{3-}$ [outer part-hexahydroxidogallium(III)] (also UHOSAN* and UHOSER*)

Mean six-coordinate Ga-OH bond distance: **1.973(6) Å** (7 structures)

b) Indium(III)

Six-coordination – hexahydroxidoindate(III)

UHORUG	2.082 Å	M. K. Kamunde-Devonish, D. B. Fast, Z. L. Mensinger, J. T. Gatlin, L. N. Zakharov, M. R. Dolgos and D. W. Johnson, *Inorg. Chem.* 2015, **54**, 3913-3920. [outer part-tetraaquadihydroxidoindium(III)]
PIVKAG	2.117 Å	F. Rominger, A. Müller and U. Thewalt, *Chem. Ber.* 1994, **127**, 797-804. (μ-hydroxido)
UHOROA	2.132 Å	M. K. Kamunde-Devonish, D. B. Fast, Z. L. Mensinger, J. T. Gatlin, L. N. Zakharov, M. R. Dolgos and D. W. Johnson, *Inorg. Chem.* 2015, **54**, 3913-3920. [outer part-tetraaquadihydroxidoindium(III)]
NONDUQ	2.139 Å	Z. L. Mensinger, J. T. Gatlin, S. T. Meyers, L. N. Zakharov, D. A. Keszler and D. W. Johnson, *Angew. Chem., Int.Ed.* 2008, ***47***, 9484-9486. (μ-hydroxido) [outer part-tetraaquadihydroxidoindium(III)]
UHORIU	2.139 Å	M. K. Kamunde-Devonish, D. B. Fast, Z. L. Mensinger, J. T. Gatlin, L. N. Zakharov, M. R. Dolgos and D. W. Johnson, *Inorg. Chem.* 2015, **54**, 3913-3920. [outer part-tetraaquadihydroxidoindium(III)]
PIVJUZ	2.152 Å	F. Rominger, A. Müller and U. Thewalt, *Chem. Ber.* 1994, **127**, 797-804. $[In(OH)_6]^{3-}$ (μ-hydroxido)
IGEHIL	2.167 Å	S. Chitsaz, T. Breyhan, J. Pauls and B. Neumüller, *Z. Anorg. Allg. Chem.* 2002, **628**, 956-964. $[In(OH)_6]^{3-}$

Mean six-coordinate In-OH bond distance: **2.160(11) Å** (2 structures)

c) Thallium(III)

Six-coordination – hexahydroxidothallate(III)

411058	2.257 Å	D. Hinz, *Z. Anorg. Allg. Chem.* 2000, **626**, 1012-1015. $Ba_2[Tl(OH)_6]OH$

d) Germanium(IV)

Six-coordination – hexahydroxidogermanate(IV)

VEGWEL	1.797 Å	A. K. Inge, J. Sun; F. Moraga, B. Guo and X. Zou, CrystEngComm 2012, ***14***, 5465-5471.
27650	1.806 Å	J. Zemann, *Neu. Jb. Mineral. Mh.* 1959, 67-69.
187162	1.897 Å	A. K. Kleppe, M. D. Welch, W. A. Crichton and A. P. Jephcoat, *Mineralog. Mag.* 2012, **76**, 949-962. $[Ge(OH)_6]^{2-}$

187161	1.899 Å	A. K. Kleppe, M. D. Welch, W. A. Crichton and A. P. Jephcoat, *Mineralog. Mag.* 2012, **76**, 949-962. $[Ge(OH)_6]^{2-}$
4295	1.900 Å	H. H. Otto, *Neu. Jb. Mineral. Abh.* 1975, **123**, 160-190. $[Ge(OH)_6]^{2-}$
NOHHOI	1.913 Å	F. Gándara, M. E. Medina, N. Snejko, B. Gómez-Lor, M. Iglesias, E. Gutiérrez-Puebla and M. A. Monge, *Inorg. Chem.* 2008, **47**, 6791-6795. $[Ge(OH)_6]^{2-}$
202596	1.914 Å	C. R. Ross, L. R. Bernstein and G. A. Waychunas, *Am. Mineralog.* 1988, **73**, 657-661. $[Ge(OH)_6]^{2-}$
15408	1.949 Å	H. Strunz and M. Giglio, *Acta Crystallogr.* 1961, **14**, 205-208.

Mean six-coordinate Ge-OH bond distance: **1.905(8) Å** (5 structures)

Six-coordination – hexanitratogermanate(IV)

EXEHEW	1.898 Å	P. Portius, B. Peerless, M. Davis and R. Campbell, *Inorg.Chem.* 2016, **55,** 8976-8984. $[Ge(NO_3)_6]^{2-}$

e) Lead(IV)

Six-coordination – hexahydroxidoplumbate(IV)

15863	2.151 Å	C. Levy-Clement and Y. Billiet, *Bull. Soc. Fr. Mineral. Cristallogr.* 1976, **99**, 361-372. $Ca[Pb(OH)_6]$
39229	2.154 Å	A. M. Il'inets, B. N. Ivanov-Emin, B. E. Zaitsev, A. V. Kostrikin, N. A. Baturin, L. L. Regel' and V. P. Dolganev, *Kristallografiya* 1990, **35**, 491-492. $K_2[Pb(OH)_6]$
92466	2.158 Å	H. Jacobs and R. Stahl, *Z. Anorg. Allgem. Chem.* 2000, **626**, 1863-1866. $K_2[Pb(OH)_6]$
15862	2.170 Å	C. Levy-Clement and Y. Billiet, *Bull. Soc. Fr. Mineral. Cristallogr.* 1976, **99**, 361-372. $Ca[Pb(OH)_6]$

Mean six-coordinate Pb-OH bond distance: **2.158(8) Å** (4 structures)

Table S6a. Six-coordinate monomethyltin(IV) structures reported in CSD (ref. 8) with remaining ligand atoms oxygen, i.e. those with an $CH_3Sn^{IV}O_5$ core.

Six-coordination

	d(Sn-CH_3)/Å	*mean d(Sn-O)/Å*	*mean d(Sn-O/C)/Å*	*Note*
JEBXAP	2.108	2.094	2.096	
1 (crystal)	2.118	2.098	2.101	See full article for EXAFS results
VACKAL	2.154	2.103	2.112	
WEYDUA	2.112	2.114	2.114	
XEMPUB	2.103	2.116	2.114	
GIBPIQ	2.129	2.117	2.119	
GIBPEM	2.120	2.118	2.118	
WEYDIO	2.143	2.118	2.122	*aka* WEYDOU
RADSAS	2.090	2.121	2.116	
ZELPEN	2.108	2.121	2.119	
Mean	*2.119*	*2.112*	*2.113*	

Table S6b. Six-coordinate dimethyltin(IV) structures reported in CSD (ref. 8) with remaining ligand atoms oxygen, i.e. those with an $(CH_3)_2Sn^{IV}O_4$ core; those with bidentate ligands exluded.

Six-coordination

	d(Sn-CH_3)/Å	*mean d(Sn-O)/Å*	*mean d(Sn-O/C)/Å*	*Note*
BAXQIB	2.092	2.175	2.147	
KURJOW	2.114	2.207	2.176	dmso
LAKNOA	2.089	2.218	2.175	
SAFMET	2.094	2.219	2.177	
GOMNUR	2.116	2.221	2.186	
HEQCIP	2.096	2.227	2.183	
DIDRAJ	2.094	2.232	2.186	
KAJVAS	2.080	2.235	2.183	
LEYFIE	2.093	2.243	2.193	
ZAXCIM	2.095	2.243	2.194	
SIFLEY	2.106	2.248	2.201	
DMTFSU	2.064	2.271	2.202	
Mean	*2.094*	*2.208*	*2.170*	

Figure S1. Unit cell packing of solid pentakis(dimethylsulfoxide)methyltin(IV) perchlorate, $[Sn(OS(CH_3)_2)_5CH_3](ClO_4)_3$, **1**. Thermal ellipsoids are set to 50 % probability. Hydrogens and the alternate positions of the oxygens for perchlorate anion 2 and 3 are not shown for clarity.

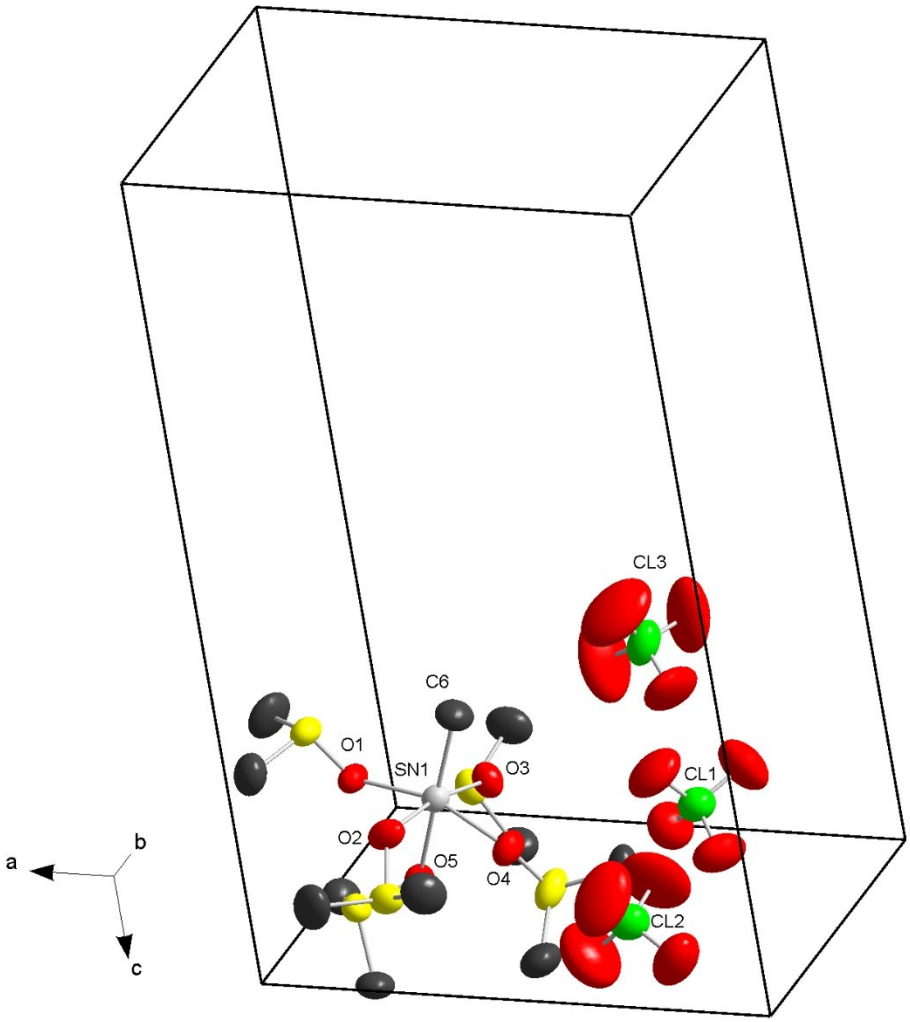

Figure S2. Tentative unit cell packing of the $[Sn_2(SH)_2(dmtf)_8]^{6+}$ entity in compound **2**. Repeating units are not shown.

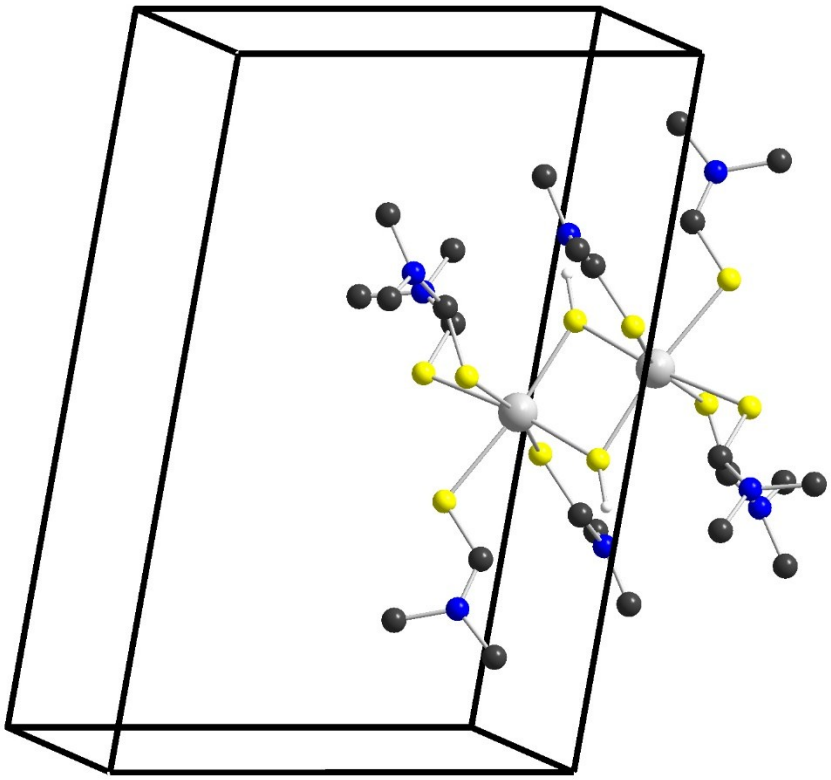

Figure S3. The experimental data (black lines) and the corresponding fits (red lines) for solid **1** (bottom; no offset) and its mother liquid (top; offset: 2 units).

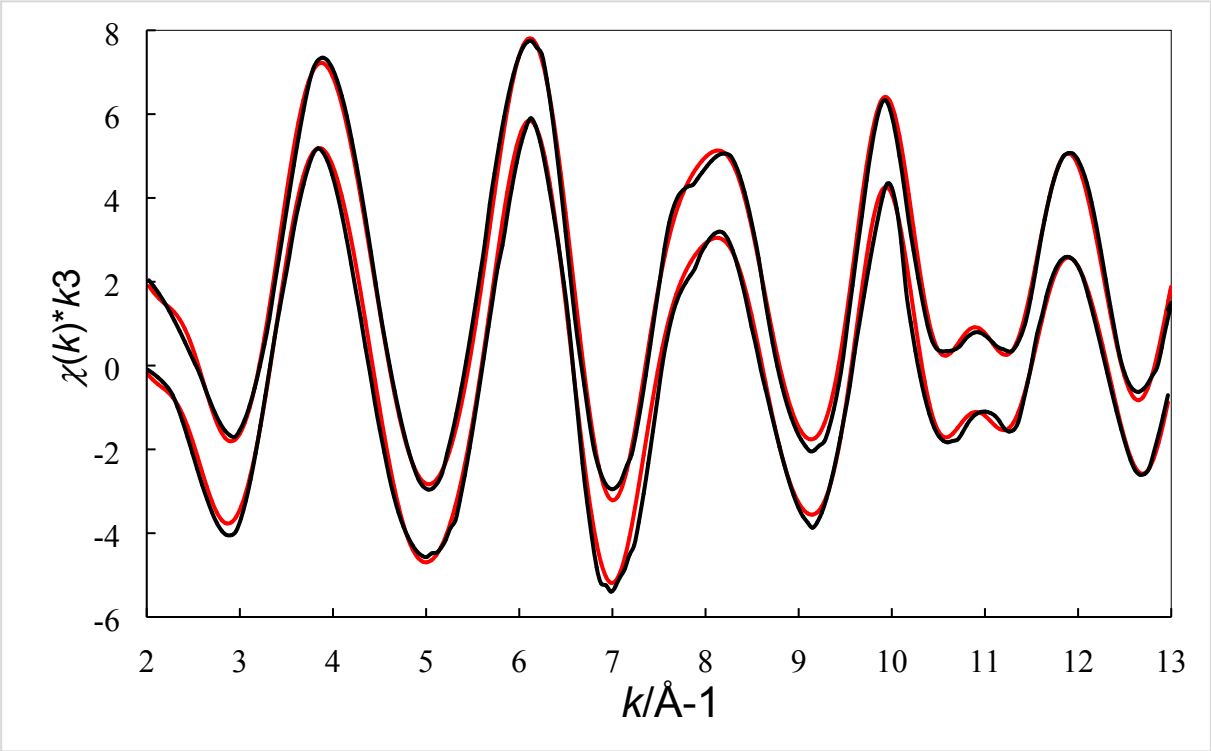

Figure S4. The Fourier transforms (FT) of the experimental data (black line) and their corresponding fits for solid **1** (bottom; no offset) and its mother liquid (top; offset: 0.5 units).