N-O ligand Supported Stannylenes: Preparation, Crystal, and Molecular Structures

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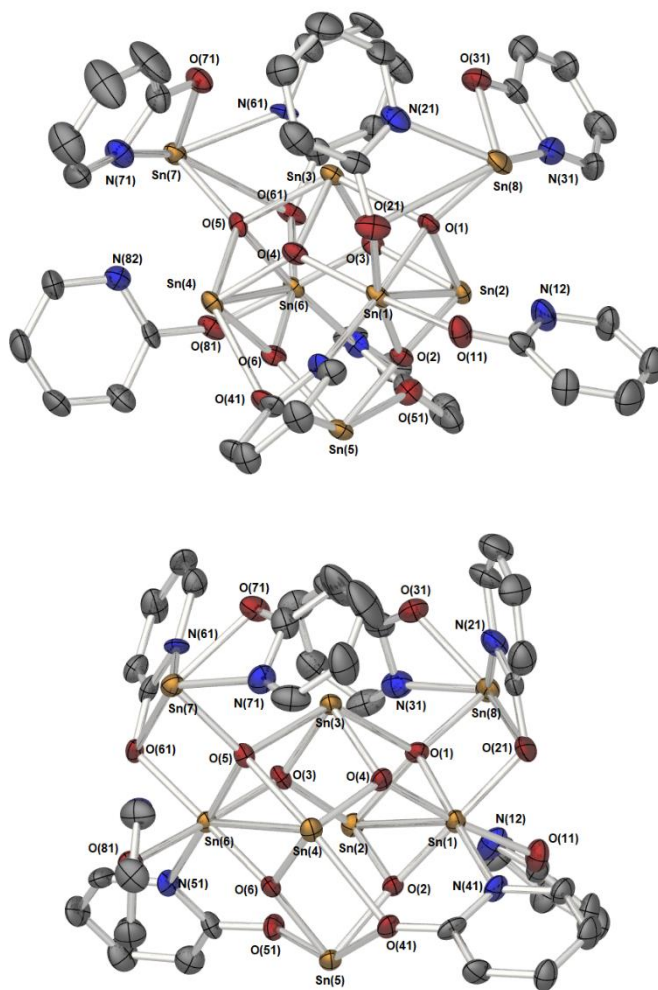
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Figure S1: Two views of the molecular structure of complex 3.

Table S1: Selected Bond lengths [Å] for Complex 3.

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Sn(1)-O(2)	2.019(6)	Sn(5)-O(2)	2.087(6)
Sn(1)-O(4)	2.046(7)	Sn(5)-O(51)	2.299(7)
Sn(1)-O(11)	2.066(7)	Sn(5)-O(41)	2.441(7)
Sn(1)-O(21)	2.084(7)	Sn(6)-O(6)	2.029(6)
Sn(1)-O(1)	2.091(6)	Sn(6)-O(3)	2.044(6)
Sn(1)-N(41)	2.178(8)	Sn(6)-O(61)	2.063(6)
Sn(2)-O(3)	2.135(7)	Sn(6)-O(81)	2.067(7)
Sn(2)-O(2)	2.146(6)	Sn(6)-O(5)	2.093(6)
Sn(2)-O(1)	2.236(7)	Sn(6)-N(51)	2.157(8)
Sn(3)-O(3)	2.135(6)	Sn(7)-O(5)	2.121(7)
Sn(3)-O(4)	2.156(6)	Sn(7)-O(71)	2.221(7)
Sn(3)-O(1)	2.378(6)	Sn(7)-N(61)	2.433(8)
Sn(3)-O(5)	2.394(6)	Sn(7)-N(71)	2.565(9)
Sn(4)-O(4)	2.099(7)	Sn(8)-O(1)	2.101(6)
Sn(4)-O(6)	2.109(6)	Sn(8)-O(31)	2.150(7)
Sn(4)-O(5)	2.253(6)	Sn(8)-N(21)	2.420(10)
Sn(4)-O(41)	2.483(7)	Sn(8)-N(31)	2.543(11)
Sn(5)-O(6)	2.086(7)		

Table S2: Selected Bond angles [°] for complex 3.

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O(2)-Sn(1)-O(4)	95.0(3)	O(51)-Sn(5)-O(41)	147.8(2)
O(2)-Sn(1)-O(11)	91.0(3)	O(6)-Sn(6)-O(3)	94.4(3)
O(4)-Sn(1)-O(11)	173.9(3)	O(6)-Sn(6)-O(61)	167.1(3)
O(2)-Sn(1)-O(21)	169.2(3)	O(3)-Sn(6)-O(61)	93.6(3)
O(4)-Sn(1)-O(21)	91.5(3)	O(6)-Sn(6)-O(81)	86.8(3)
O(11)-Sn(1)-O(21)	82.5(3)	O(3)-Sn(6)-O(81)	177.8(3)
O(2)-Sn(1)-O(1)	82.5(3)	O(61)-Sn(6)-O(81)	84.9(3)
O(4)-Sn(1)-O(1)	81.9(3)	O(6)-Sn(6)-O(5)	81.3(3)
O(11)-Sn(1)-O(1)	98.1(3)	O(3)-Sn(6)-O(5)	81.8(2)
O(21)-Sn(1)-O(1)	89.8(3)	O(61)-Sn(6)-O(5)	89.8(3)
O(2)-Sn(1)-N(41)	100.1(3)	O(81)-Sn(6)-O(5)	96.6(3)
O(4)-Sn(1)-N(41)	95.6(3)	O(6)-Sn(6)-N(51)	102.5(3)
O(11)-Sn(1)-N(41)	84.0(3)	O(3)-Sn(6)-N(51)	94.6(3)
O(21)-Sn(1)-N(41)	87.9(3)	O(61)-Sn(6)-N(51)	86.9(3)
O(1)-Sn(1)-N(41)	176.6(3)	O(81)-Sn(6)-N(51)	86.9(3)
O(3)-Sn(2)-O(2)	92.6(2)	O(5)-Sn(6)-N(51)	175.0(3)
O(3)-Sn(2)-O(1)	77.5(2)	O(5)-Sn(7)-O(71)	88.2(3)
O(2)-Sn(2)-O(1)	76.4(2)	O(5)-Sn(7)-N(61)	80.8(3)
O(3)-Sn(3)-O(4)	94.0(3)	O(71)-Sn(7)-N(61)	78.5(3)
O(3)-Sn(3)-O(1)	74.5(2)	O(5)-Sn(7)-N(71)	80.4(3)
O(4)-Sn(3)-O(1)	73.3(2)	O(71)-Sn(7)-N(71)	55.6(3)
O(3)-Sn(3)-O(5)	73.2(2)	N(61)-Sn(7)-N(71)	130.5(3)
O(4)-Sn(3)-O(5)	74.1(2)	O(1)-Sn(8)-O(31)	90.1(3)
O(1)-Sn(3)-O(5)	131.6(2)	O(1)-Sn(8)-N(21)	80.6(3)
O(4)-Sn(4)-O(6)	93.2(3)	O(31)-Sn(8)-N(21)	79.2(3)
O(4)-Sn(4)-O(5)	78.3(2)	O(1)-Sn(8)-N(31)	83.4(3)
O(6)-Sn(4)-O(5)	75.9(2)	O(31)-Sn(8)-N(31)	56.7(3)
O(4)-Sn(4)-O(41)	81.0(2)	N(21)-Sn(8)-N(31)	132.8(3)
O(6)-Sn(4)-O(41)	71.2(2)	C(15)-N(12)-C(11)	120.0(10)
O(5)-Sn(4)-O(41)	139.8(2)	C(25)-N(21)-C(21)	120.1(10)
O(6)-Sn(5)-O(2)	91.4(2)	C(25)-N(21)-Sn(8)	120.9(8)
O(6)-Sn(5)-O(51)	84.4(2)	C(21)-N(21)-Sn(8)	118.7(7)
O(2)-Sn(5)-O(51)	76.2(2)	C(35)-N(31)-C(31)	118.9(11)
O(6)-Sn(5)-O(41)	72.4(2)	C(35)-N(31)-Sn(8)	156.1(8)
O(2)-Sn(5)-O(41)	82.2(2)	C(31)-N(31)-Sn(8)	84.6(7)

C(45)-N(41)-C(41)	119.4(9)	Sn(3)-O(3)-Sn(2)	109.7(3)
C(45)-N(41)-Sn(1)	121.4(7)	Sn(1)-O(4)-Sn(4)	128.2(3)
C(41)-N(41)-Sn(1)	119.2(6)	Sn(1)-O(4)-Sn(3)	106.8(3)
C(51)-N(51)-C(55)	119.9(8)	Sn(4)-O(4)-Sn(3)	110.2(3)
C(51)-N(51)-Sn(6)	119.6(6)	Sn(6)-O(5)-Sn(7)	114.8(3)
C(55)-N(51)-Sn(6)	120.4(7)	Sn(6)-O(5)-Sn(4)	97.8(3)
C(61)-N(61)-C(65)	118.7(9)	Sn(7)-O(5)-Sn(4)	129.8(3)
C(61)-N(61)-Sn(7)	115.1(6)	Sn(6)-O(5)-Sn(3)	97.3(2)
C(65)-N(61)-Sn(7)	125.4(7)	Sn(7)-O(5)-Sn(3)	113.9(3)
C(75)-N(71)-C(71)	119.8(10)	Sn(4)-O(5)-Sn(3)	97.3(2)
C(75)-N(71)-Sn(7)	154.9(9)	Sn(6)-O(6)-Sn(5)	125.5(3)
C(71)-N(71)-Sn(7)	85.3(6)	Sn(6)-O(6)-Sn(4)	104.7(3)
C(81)-N(82)-C(85)	118.9(9)	Sn(5)-O(6)-Sn(4)	119.7(3)
Sn(1)-O(1)-Sn(8)	116.6(3)	C(11)-O(11)-Sn(1)	126.6(6)
Sn(1)-O(1)-Sn(2)	97.8(3)	C(21)-O(21)-Sn(1)	127.6(6)
Sn(8)-O(1)-Sn(2)	121.2(3)	C(31)-O(31)-Sn(8)	103.9(7)
Sn(1)-O(1)-Sn(3)	97.9(2)	C(41)-O(41)-Sn(5)	131.4(7)
Sn(8)-O(1)-Sn(3)	120.3(3)	C(41)-O(41)-Sn(4)	124.3(6)
Sn(2)-O(1)-Sn(3)	98.3(2)	Sn(5)-O(41)-Sn(4)	94.9(2)
Sn(1)-O(2)-Sn(5)	128.1(3)	C(51)-O(51)-Sn(5)	136.4(6)
Sn(1)-O(2)-Sn(2)	103.1(3)	C(61)-O(61)-Sn(6)	124.3(5)
Sn(5)-O(2)-Sn(2)	117.8(3)	C(71)-O(71)-Sn(7)	102.8(7)
Sn(6)-O(3)-Sn(3)	107.7(3)	C(81)-O(81)-Sn(6)	123.4(6)
Sn(6)-O(3)-Sn(2)	128.3(3)		

Table S3: Crystal data and structure refinement for complexes 1-5.

| Compound reference	1	2	3	4	5
Chemical formula	$C_{22}H_{44}N_4O_2Si_4Sn_2$	$C_{40}H_{32}N_8O_8Sn_4$	$2(C_{40}H_{32}N_8O_{14}Sn_8) \cdot 3(C_7H_8)$	$C_{18}H_{12}N_2O_2Sn$	$2(C_{26}H_{16}N_2O_2Sn) \cdot C_7H_8$
Formula Mass	746.35	1227.49	3872.91	406.99	1106.33
Crystal system	Triclinic	Monoclinic	Triclinic	Orthorhombic	Triclinic
a/Å	9.15330(10)	23.8105(6)	10.5700(4)	9.9047(3)	8.9889(4)
b/Å	12.9058(2)	7.97210(10)	15.3188(9)	11.9296(4)	10.9833(5)
c/Å	15.4088(2)	25.2769(7)	18.9698(7)	12.8849(4)	12.4588(4)
α/°	111.6830(10)	90	98.192(4)	90	86.532(3)
β/°	98.2530(10)	118.745(4)	102.401(4)	90	85.348(3)
γ/°	95.3780(10)	90	103.735(4)	90	67.035(4)
Unit cell volume/Å³	1652.48(4)	4206.8(2)	2852.9(2)	1522.47(8)	1128.25(9)
Temperature/K	150(2)	150(2)	150(2)	150(2)	150(2)
Space group	$P\bar{1}$	$I2/a$	$P\bar{1}$	$Pbcn$	$P\bar{1}$
No. of formula units per unit cell, Z	2	4	1	4	1
No. of reflections measured	56287	13784	20363	11655	9114
No. of independent reflections	6562	4131	11091	1739	4563
R_{int}	0.0444	0.0639	0.0595	0.0319	0.0265
Final R_1 values ($I > 2\sigma(I)$)	0.0242	0.0454	0.0654	0.0237	0.0275
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0688	0.1191	0.1827	0.0485	0.0534
Final R_1 values (all data)	0.0247	0.0474	0.0768	0.0345	0.0309
Final $wR(F^2)$ values (all data)	0.0694	0.1208	0.1985	0.0531	0.0549
Goodness of fit	1.090	1.074	1.040	1.089	1.057
CCDC number	2015978	2015979	2015980	2015981	2015982

DOSY NMR Studies of 2:

[Sn(OPy)$_2$]$_4$ (**2**)

Solid state structure in solution is a tetramer.

^{119}Sn, ^{1}H and ^{13}C all show only one peak in C$_6$D$_6$ at RT.

DOSY NMR also shows only one set of resonances
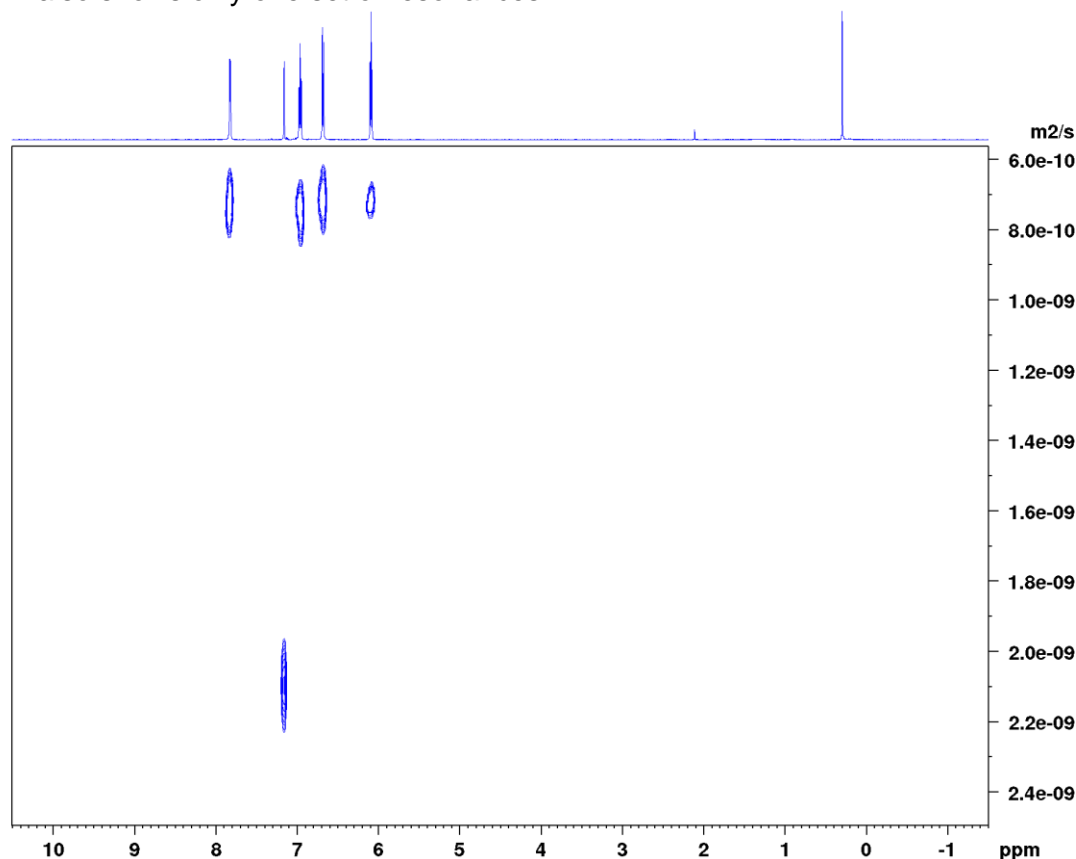
Measured diffusion coefficient = 6.87 x10^{-10} s^{-1}
Based on the Stokes Einstein equation (below) this corresponds to a hydrodynamic radius of 4.95 Å.

$$D = \frac{kT}{6\pi\eta r_H}$$

The crystal structure ASU has two Sn centres, corresponding to a molecular volume of 367.7 Å^3. This gives a radius of 4.44 Å, assuming a spherical system
The full tetrameric solid-state structure has a molecular volume of 721.36 Å^3, corresponding to a radius of 5.56 Å.

Assuming a spherical system, the hydrodynamic radius empirically determined corresponds to a volume of 509 Å^3. With each Sn "unit" occupying approx. 183 Å^3,* the empirical value corresponds to what is likely a trimeric system, however, we believe that an equilibrium between the tetrameric and dimeric species (such that we

observe one set of resonances in the 1H, 13C and 119Sn and an average diffusion coefficient), is more likely in the solution state.
*Based on the ASU dimer and grown tetramer, 368/2=184 and 721/4=180

Using Stalke's method[1,2], which we correct empirically for molecular density[3] (and hence accounting for the heavy Sn atom), we predict a molecular mass of 937 Da (c.f. a calculated mass for a trimeric species $[Sn(OPy)_2]_3$ of 921 Da, 2% error). This uses an empirically determined density correction factor of 1.5535.[3]

This again supports the assertation that we observe exchange between a dimeric and tetrameric species (as is chemically more likely than the trimer). This is based on big assumptions though as Stalke's method has not been reported for Sn before, there is some work on lanthanide phosphnoate species though.[4]

1. Neufeld, Stalke, *Chem. Sci.*, 2015, **6**, 3354-3364
2. Bachmann, Gernert, Stalke, *Chem. Comm.* 2016, **52**, 12861-12864
3. Kreyenschmidt, Bachmann, Niklas, Stalke, *Chemistry Select*, 2017, **2**, 6957-6960
4. Koehne, Gerstel, Bruhn, Reithmaier, Benyoucef, Pietschnig, *Inorg. Chem.*, 2021, 60, 5297-5309

VT DOSY NMR studies of 2

Spectra all run in toluene.

Possible to calculate hydrodynamic radius and therefore, assumed spherical volume. Not possible to use Stalke's method as we have heavy atoms, and the empirical correction needed has only been determined in C_6D_6 and THF.

All calculations based on the Stokes-Einstein equation:

$$D = \frac{kT}{6\pi\eta r_H}$$

Toluene viscosity determined based on empirical estimation as per reference. Equation is as follows

$$\ln(\eta^*) = -5.2203 + \frac{8.964}{T^*} - \frac{5.834}{(T^*)^2} + \frac{2.089}{(T^*)^3}$$

Where η^* and T^* are dimensionless variables, defined as:

$$T^* = \frac{T}{298.15}$$

$$\eta^* = \frac{\eta(T)}{\eta(298.15)}$$

$$\eta(298.15) = 554.2 \pm 3.3 \; \mu Pa \, s$$

This gives the data in the table, which is then plotted in the graphs below. Both graphs show that as a function of temperature the hydrodynamic radius reduces, suggesting that the equilibrium discussed previously shifts more towards the dimeric species as a function of temperature. At the highest temperatures the trend appears to level off, with the hydrodynamic radius being ~ that of the dimeric species we'd expect (4.44 Å), suggesting at these temperatures the equilibrium has shifted almost fully to the dimeric species.

| T / K	D_x / s^{-1}	Hydrodynamic Radii / Å	Expected Volume / Å^3
298	7.97*10^{-10}	4.934255	503.214668
308	9.42*10^{-10}	4.84727	477.067886
318	1.12*10^{-10}	4.703578	435.886865
328	1.31*10^{-9}	4.571166	400.100898
338	1.54*10^{-9}	4.41312	360.019436
348	1.75*10^{-9}	4.370032	349.576597
328	1.29*10^{-9}	4.647183	420.395366
328	1.27*10^{-9}	4.704556	436.158581
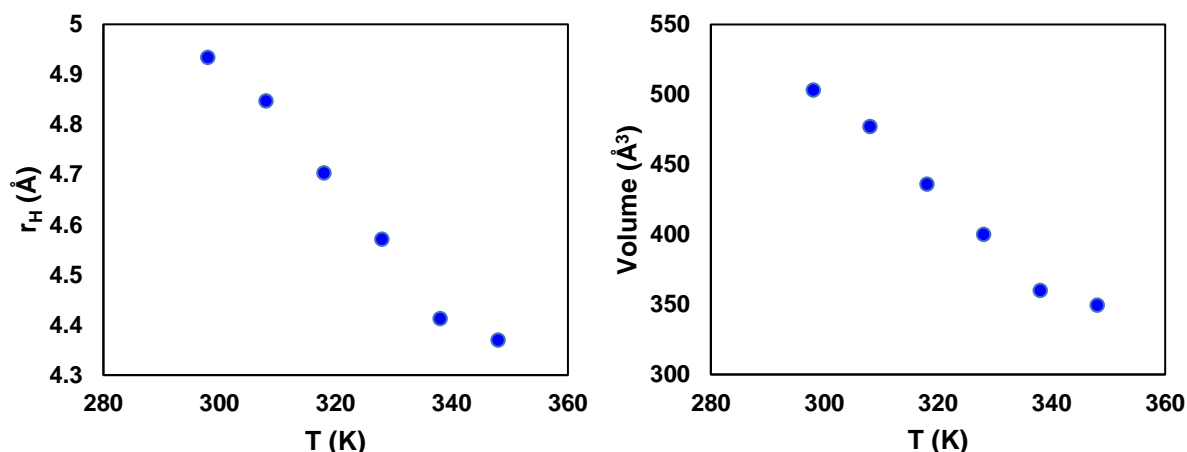
From this, we have used expected diffusion coefficients to calculate an estimated equilibrium constant (working as for the phosphate stuff and is all in the spreadsheet. This then gives the data below, and the plot below.

T / K	K
298	20.01007543
308	33.88393885
318	86.37062653
328	266.371416
338	-2133.662168
348	-938.8074633

We can then plot LN(K) against 1/T (the Van t'hoff equation)
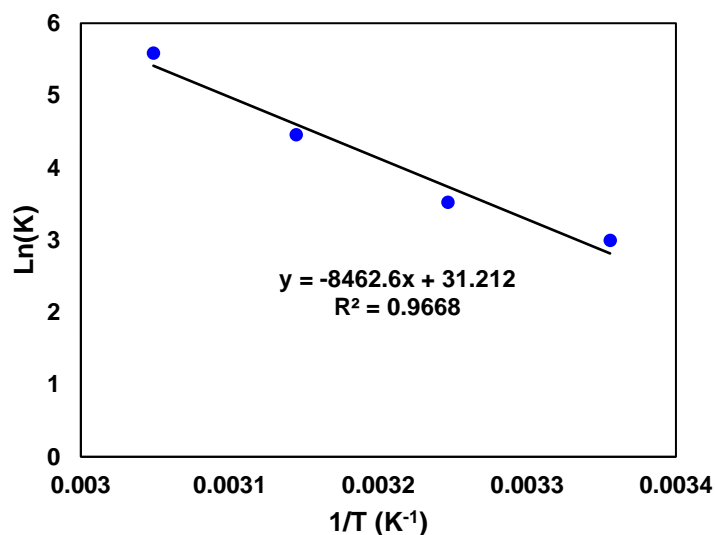
Then, based on the following equations thermodynamic parameters can be determined:

$$\Delta H = -m \times R = 70.4 \ (\pm 9.22) \ kJ \ mol^{-1}$$

$$\Delta S = c \times R = 259 \ (\pm 29.5) \ J \ K^{-1} mol^{-1}$$

$$\Delta G = \Delta H - T\Delta S = -6.97 \ (\pm 12.7) \ kJ \ mol^{-1}$$