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ARTICLE TYPE

ELECTRONIC SUPPORTING INFORMATION

Structure Analysis of Mixtures with Ultrafast Two-Dimensional Infrared Spectroscopy

Andreas T. Messmer,[a] Katharina M. Lippert,[b] Peter R. Schreiner,[b] and Jens Bredenbeck*[a,c]

Contents

A. NMR spectra of the 1:1 mixture

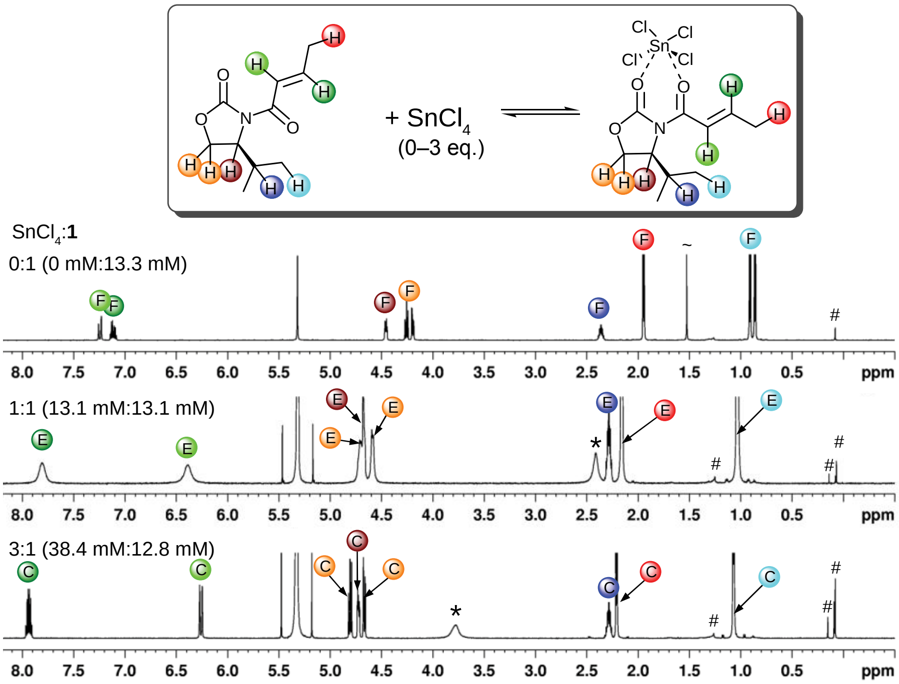


Fig. S1 ^{1}H-NMR (600 MHz, 298 K, solvent CD_2Cl_2) titration experiment of **1** with increasing amounts of $SnCl_4$ in CH_2Cl_2.

The ^{1}H-NMR spectra of free **1** (top), a 1:1 mixture of **1** and $SnCl_4$ (middle) and a 3:1 mixture of **1** and $SnCl_4$ (bottom) are compared in Fig. S1. The spectrum of the 1:1 mixture shows broadened signals and can be understood as a motional average of the spectrum of free **1** (top) and the **1**·$SnCl_4$ (bottom). Since the exchange between **1** and **1**·$SnCl_4$ is faster than the inherent time resolution of the NMR experiment, the two species cannot be detected individually in a 1:1 mixture under these conditions (fast exchange limit). From this experiment being in the fast exchange regime one can estimate the exchange rate between **1** and **1**·$SnCl_4$ to be faster than 1.3 ms^{-1}.

The ^{1}H-NMR spectrum for a 3:1 mixture is well resolved with narrow peaks of **1**·$SnCl_4$. There is no evidence for the presence of additional complexes that are seen in the P2D-IR experiments. This is caused by the limited sensitivity of the NMR technique. Additionally, fast exchange between the various complexes is likely, which makes the detection of additional species present in low concentrations with NMR even more difficult, if not impossible.

The additional signals in the NMR spectrum are caused by grease (#), water (~), hydrolyzed $SnCl_4$ (*), $CHDCl_2$ (5.3 ppm), and the signals at 5.2 ppm and 5.5 ppm are due to coupling to ^{13}C in dichloromethane

The ^{1}H-NOESY spectrum of the 1:1 mixture also shows the motionally averaged NOESY spectrum of the interconverting species.[1] The presence of a NOESY cross peak implies that in at least one of the species there is an interaction between the two connected nuclei. It does not tell us, however, which of the species causes the signal.

Based on these results and due to the low inherent time resolution it is not possible to determine the structure of both species under these conditions based on NMR techniques.

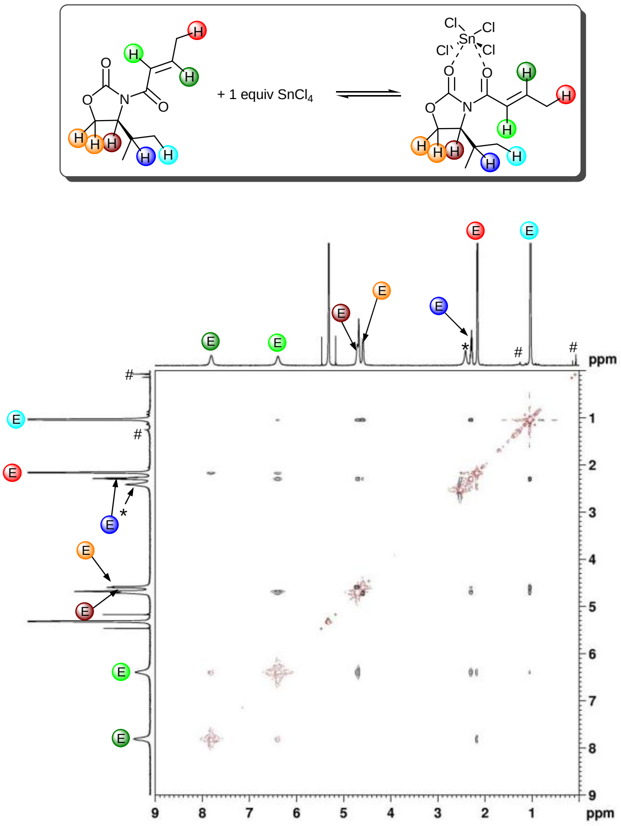


Fig. S2 ^{1}H-NOESY (600 MHz, 298 K) spectrum of a 1:1 mixture of **1** (13.1 mM) and $SnCl_4$ (13.1 mM) in CH_2Cl_2.

B. Determination of the systematic error caused by rotational diffusion

Table S1 Detailed comparison of the determined anisotropies and angles for **1**.

Peak	ν_2/ν_2 (Fig.1 pos. 1)	ν_1/ν_2 (Fig.1 pos. 3)	ν_1/ν_3 (Fig.1 pos. 4)	ν_2/ν_3 (Fig.1 pos. 2)
Fitted time dependence of the anisotropy				
Anisotropy extrapolated to 0 ps	0.411(3)	−0.020(5)	0.273(8)	0.117(4)
Determined angle (°)	–[a]	57 ± 2	27 ± 3	43 ± 2
Anisotropy fitted at 1.5 ps	0.365(2)	−0.025(3)	0.253(4)	0.102(2)
Determined angle (°)	14 ± 4	57 ± 2	30 ± 2	45 ± 2
Systematic error (°)	14	0	3	2
Annihilation method				
$\Delta\alpha_{\parallel}/\Delta\alpha_{\perp}$ measured at 1.5 ps	2.75 ± 0.15	0.85 ± 0.15	2.0 ± 0.25	1.3 ± 0.05
Calculated anisotropy	0.37 ± 0.02	−0.05 ± 0.06	0.25 ± 0.05	0.09 ± 0.02
Determined angle (°)	13 ± 5	60 ± 7	30 ± 5	46 ± 2

[a] Not determinable. Since the two pulses interact with the very same transition dipole moment, the real angle is 0°.

Table S2 Detailed comparison of the determined anisotropies and angles for **1**·$SnCl_4$.

Peak	ν'_1/ν'_1 (Fig.1 pos. I)	ν'_1/ν'_2 (Fig.1 pos. III)	ν'_1/ν'_3 (Fig.1 pos. IV)	ν'_2/ν'_3 (Fig.1 pos. II)
Fitted time dependence of the anisotropy				
Anisotropy extrapolated to 0 ps	0.403(9)	0.340(5)	0.086(2)	0.069(3)
Determined angle (°)	0 ± 7	18 ± 4	46 ± 2	48 ± 2
Anisotropy fitted at 1.5 ps	0.390(5)	0.319(3)	0.0804(10)	0.056(2)
Determined angle (°)	7 ± 5	22 ± 3	47 ± 2	49 ± 2
Systematic error (°)	7	4	1	1
Annihilation method				
$\Delta\alpha_{\parallel}/\Delta\alpha_{\perp}$ measured at 1.5 ps	2.75 ± 0.15	2.75 ± 0.25 [a]	1.3 ± 0.05	1.2 ± 0.05
Calculated anisotropy	0.37 ± 0.02	0.36 ± 0.04	0.09 ± 0.02	0.06 ± 0.02
Determined angle (°)	13 ± 5	15 ± 8	46 ± 2	49 ± 2

[a] Between 2.35 and 2.85.

Tables S1 and S2 compare the angles determined by the anisotropy and the annihilation method. The systematic error at a delay time of 1.5 ps induced by the rotation of the molecules in solution was calculated by comparing the anisotropy at t = 0 ps obtained by extrapolation with the fitted anisotropy at t = 1.5 ps. It is apparent that the systematic error is largest for the diagonal peak, *i.e.*, small angles between the involved transition dipole moments, and, as expected, drops significantly with increasing angles. For angles larger than 20° the observed systematic error is at maximum 3°. From a theoretical point of view, the systematic error disappears for magic angles and for slow rotational diffusion. Within the experimental errors, the angles deduced from the fitted anisotropy at t = 1.5 ps and deduced by annihilating the cross peaks using the spectra measured with parallel and perpendicular polarization at a delay time of t = 1.5 ps are the same.

C. Comparison of the experimental and computed frequencies

Table S3 Comparison of the experimentally determined vibrational energies of **1** in CH_2Cl_2 with the results of DFT computations (M06/6−31+G(*d*,*p*)/PCM/Bondi).

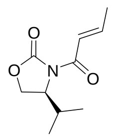
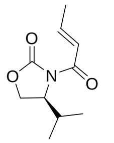
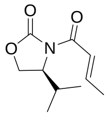
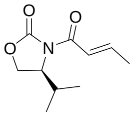
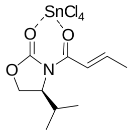
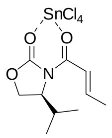
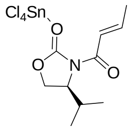
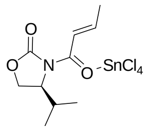
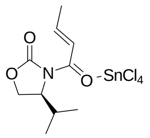
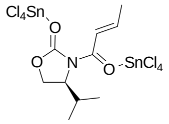
vibration	experiment (cm^{-1})	 **1-apc** (cm^{-1})	 **1-apt** (cm^{-1})	 **1-spt** (cm^{-1})	 **1-spc** (cm^{-1})
ν_1	1638	1694 (Δ = 56)	1714 (Δ = 76)	1717 (Δ = 79)	1703 (Δ = 65)
ν_2	1686	1741 (Δ = 55)	1735 (Δ = 49)	1742 (Δ = 56)	1744 (Δ = 58)
ν_3	1777	1831 (Δ = 54)	1836 (Δ = 59)	1847 (Δ = 70)	1857 (Δ = 80)

Table S4 Comparison of the experimentally determined vibrational energies of **1**·$SnCl_4$ in CH_2Cl_2 with the results of DFT computations (M06/6-31+G(*d*,*p*)/SDD/PCM/Bondi).

vibration	experiment [a] (cm^{-1})	 **1-spc**-*κ*²*O*,*O′* (cm^{-1})	 **1-spt**-*κ*²*O*,*O′* (cm^{-1})	 **1-apc**-*κO* (cm^{-1})	 **1-apc**-*κO′* (cm^{-1})	 **1-apt**-*κO′* (cm^{-1})	 **1-apc**-1*κO*,2*κO′* (cm^{-1})
ν'_1	1567	1617 (Δ = 50)	1634 (Δ = 67)	1691 (Δ = 124)	1576 (Δ = 9)	1581 (Δ = 14)	1606 (Δ = 39)
ν'_2	1633	1687 (Δ = 54)	1710 (Δ = 77)	1724 (Δ = 91)	1696 (Δ = 63)	1709 (Δ = 76)	1693 (Δ = 60)
ν'_3	1727	1780 (Δ = 53)	1776 (Δ = 49)	1766 (Δ = 39)	1859 (Δ = 132)	1865 (Δ = 138)	1768 (Δ = 41)

[a] for the major complex.

The comparison of computed and measured vibrational energies is shown in Table S3 for **1** and S4 for **1**·$SnCl_4$. The computed energies are not scaled because there is no scaling factor available for the M06 functional in combination with the 6-31+G(*d*,*p*) basis set. The experimental results for **1** are best matched by the computation for **1-apc**. For this conformer, the computed vibrational energies of the carbonyl and alkenyl vibrations are all shifted by the same value of about 55 cm^{-1}, which means that a uniform scaling by 0.97 would make the computed spectrum coincide with the experimental one. For the other conformers the shifts relative to experiment strongly depend on the mode. From this one can conclude that conformer **1-apc** is present in solution. This is in agreement with the conclusion drawn by the P2D-IR experiments and the comparison of the computed and measured angles between the transition dipole moments.

For the tin complex, the chelate **1-spc**-*κ*²*O*,*O′*·$SnCl_4$ matches experiment best, with a uniform correction for all three modes of about 52 cm^{-1}. This assignment is also in accordance with the angle measurements.

D. Discussion of the signals possibly originating from 1-spt-κ^2*O*,*O′*·SnCl$_4$

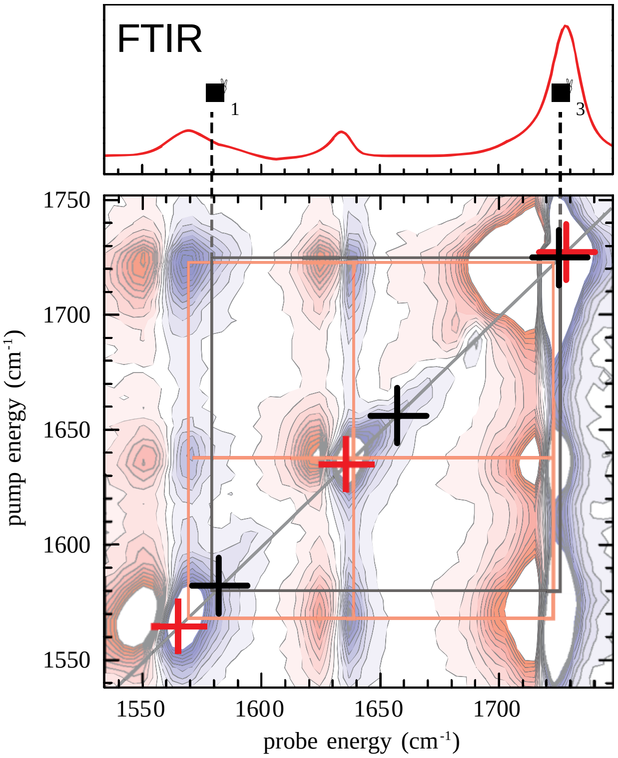


Fig. S3 Comparison of the computed vibrational energies for **1-spc**-κ^2*O*,*O′*·SnCl$_4$ (red) and **1-spt**-κ^2*O*,*O′*·SnCl$_4$ (black) with the P2D-IR spectrum (parallel polarization). All computed energies are shifted by 52 cm^{-1}.

Figure S3 compares the computed vibrational energies for the major conformer in solution (**1-spc**-κ^2*O*,*O′*·SnCl$_4$, red crosses) and the computed vibrational energies of **1-spt**-κ^2*O*,*O′*·SnCl$_4$ (black crosses) with the experimental P2D-IR spectrum. At all computed signal positions of conformer **1-spt**-κ^2*O*,*O′*·SnCl$_4$ there are signals on the diagonal in the spectrum. Assuming that (only) **1-spt**-κ^2*O*,*O′*·SnCl$_4$ causes these signals, the population of this conformer can be estimated by the signal size to be less than 15%. The position of the bands (black crosses) also fit well to the coupling pattern found for the minor species (highlighted by the black grid, *cf.* Fig. 4 in the main text). In the experiment, we find that the angle between the transition dipole moments of the low and high energy vibration (v^{A}_{1} and v^{A}_{3}) is at least 5° smaller for the minor species than for the major conformer. The computation yields an angle of 20° for **1-spt**-κ^2*O*,*O′*·SnCl$_4$, which is 26° smaller than for the major conformer. So also the smaller angle is reproduced by the computation. Unfortunately, the cross peaks to the vibration around 1658 cm^{-1} are not reliably seen. This can be caused by the weak intensity of the signals in combination with strong overlapping effects and similar angles to the major species. The respective angles computed for **1-spt**-κ^2*O*,*O′*·SnCl$_4$ only vary by less than 10° from the ones measured for the major species.

In conclusion, the observed signals can be explained by the presence of the chelate **1-spt**-κ^2*O*,*O′*·SnCl$_4$ in low concentrations. Experiments with higher spectral resolution and more infrared excitation power could possibly identify the minor species unequivocally by detecting all cross peaks and allowing more precise measurements of the angles.

E. P2D-IR spectra for high excess of $SnCl_4$

Table S5 Determination of the angles based on the annihilation method for the species formed at high excess of $SnCl_4$

	ν'_2/ν'_2	ν'_1/ν'_2	ν^C_1/ν^C_3	ν^C_2/ν^C_3
$\Delta\alpha_\parallel/\Delta\alpha_\perp$ measured at 1.5 ps	2.85 ± 0.1	2.7 ± 0.1	0.95 ± 0.2	1.15 ± 0.2
Calculated anisotropy	0.38 ± 0.02	−0.36 ± 0.02	−0.02 ± 0.07	0.04 ± 0.06
Determined angle (°)	10 ± 5	15 ± 4	56 ± 8	50 ± 6

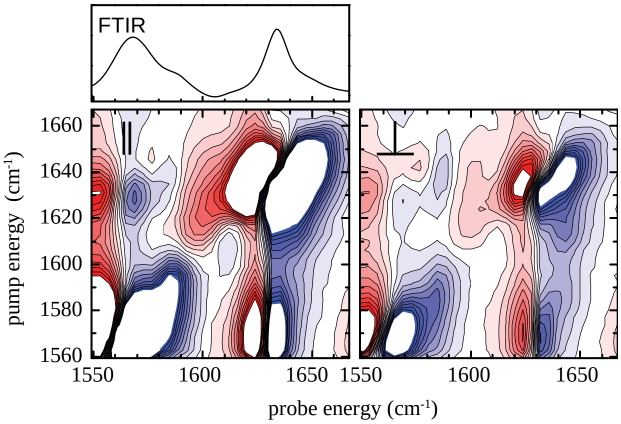


Fig. S4 P2D-IR spectrum for parallel (left) and perpendicular polarization (right) of a mixture of **1** (28 mM) and $SnCl_4$ (531 mM) in CH_2Cl_2 (1.5 ps). The contour lines are spaced by 0.03 mOD. Signals larger than ±0.3 mOD are truncated. The FTIR spectrum of the sample is shown in the top panel for reference.

F. NMR spectra for high excess of $SnCl_4$

The ^{1}H-NOESY spectrum of the sample with large excess of $SnCl_4$ shows only signatures of the major conformer. In contrast to the P2D-IR spectra, there is no evidence for an additional species present in solution. The spectrum is basically identical to the one measured for a 3:1 ($SnCl_4$:**1**) mixture.[1] The difference between the number of species observed in P2D-IR and ^{1}H-NOESY could be caused both by a lower sensitivity of the NMR measurement or by fast exchange.

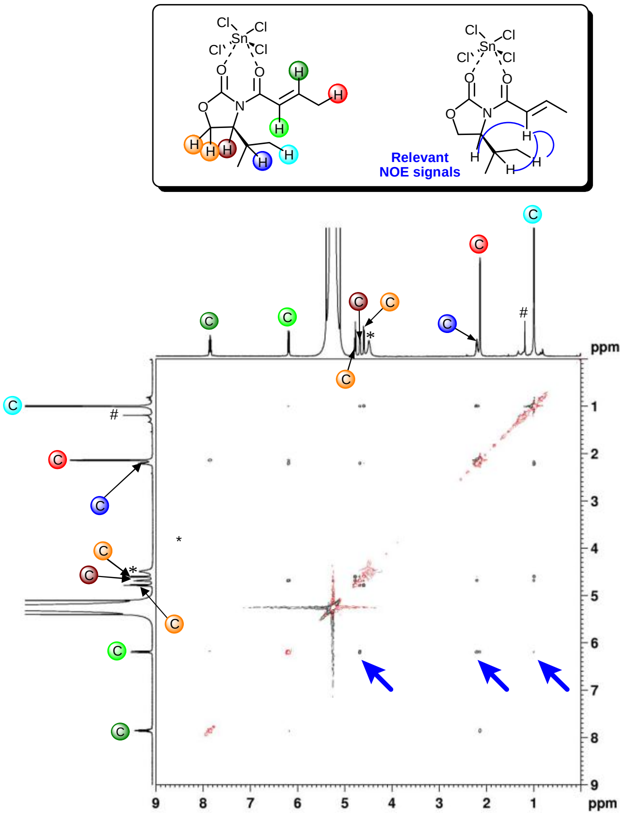


Fig. S5 ^{1}H-NOESY (600 MHz, 298 K) spectrum of a mixture of **1** (28 mM) and $SnCl_4$ (530 mM) in CD_2Cl_2.

G. Computational Details

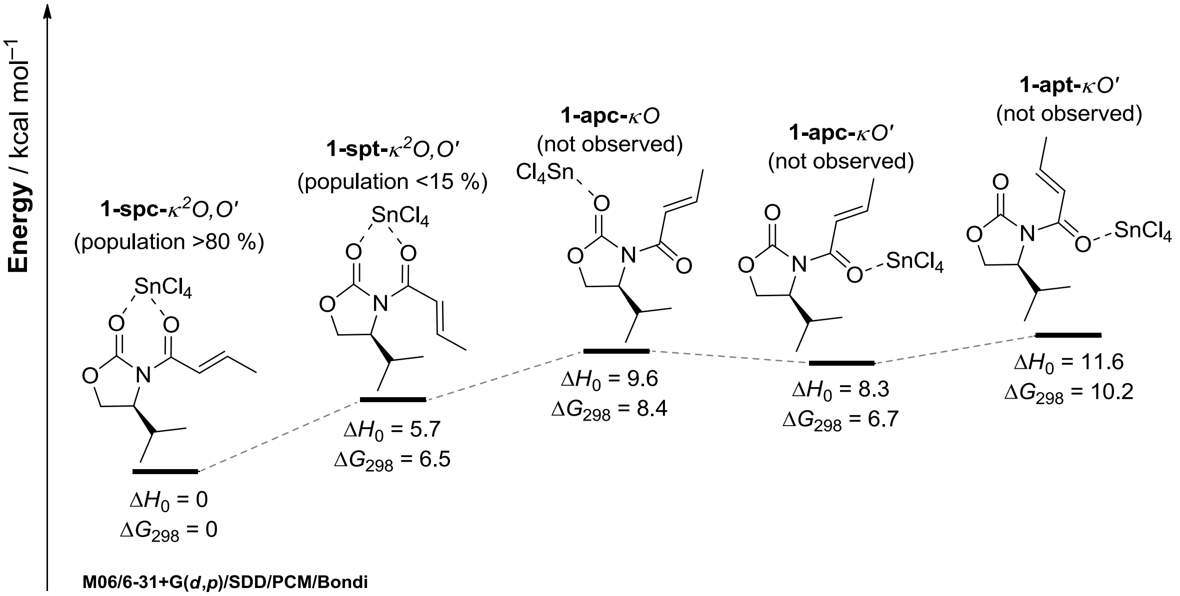


Fig. S5 Complex species of **1·SnCl$_4$**, computed at M06/6-31+G(*d*,*p*)/SDD/PCM/Bondi level of theory. The population was determined before (*cf.* Chapter D).

Table S6 Summary of the DFT computations (M06/6-31+G(*d*,*p*)/SDD/PCM/Bondi) for **1-apc** and SnCl$_4$.

	Energy (–au)	ZPVE (au)	E+ZPVE (–au)	G_{298} (–au)
1-apc	670.1735607	0.2420735	669.9314872	669.972935
SnCl$_4$	1844.1835748	0.0042299	1844.1793449	1844.213512

Table S7 Summary of the DFT computations M06/6-31+G(*d*,*p*)/SDD/PCM/Bondi for the various tin complexes of **1**. A corresponding summary for free **1** can be found in reference 1.

Complex	Energy (–au)	ZPVE (au)	E+ZPVE (–au)	ΔH_0 (kcal mol^{-1})	D_0 (kcal mol^{-1})	G_{298} (–au)	ΔG_{298} (kcal mol^{-1})	D_{298} (kcal mol^{-1})
1-spc-κ^2O,O'	2514.3822548	0.2487101	2514.1335447	0.0	14.3	2514.188673	0.0	1.4
1-spt-κ^2O,O'	2514.3736469	0.2492156	2514.1244313	5.7	8.5	2514.178317	6.5	–5.1
1-apc-κO	2514.3662503	0.2480162	2514.1182341	9.6	4.6	2514.175284	8.4	–7.0
1-apc-$\kappa O'$	2514.3682351	0.2478529	2514.1203822	8.3	6.0	2514.178005	6.7	–5.3
1-apt-$\kappa O'$	2514.3627043	0.2476434	2514.1150609	11.6	2.7	2514.172395	10.2	–8.8
1-apc-1κO,2$\kappa O'$	4358.5730877	0.2550642	4358.3180235	–	17.5	4358.388755	–	–7.0

Cartesian Coordinates

M06/6-31+ G(*d*,*p*)/SDD/PCM/BONDI

1-spc-κ^{2}*O,O'*

atomic number	X(Å)	Y(Å)	Z(Å)
8	0.027294	-0.032593	0.045035
6	-0.011578	-0.010689	1.274683
8	1.089389	-0.010320	1.980682
6	0.781384	0.154702	3.389009
6	-0.694906	-0.213824	3.505867
1	1.450556	-0.500425	3.948372
1	0.980989	1.198280	3.641830
1	-1.199613	0.512458	4.150898
7	-1.122768	0.003328	2.097818
6	-2.426086	0.157326	1.663949
6	-3.468589	0.261985	2.660101
6	-4.761460	0.298102	2.279418
1	-3.205884	0.308420	3.712903
1	-4.987431	0.234044	1.213769
6	-5.900805	0.414523	3.209742
1	-6.578084	-0.439135	3.080286
1	-5.584730	0.471248	4.255214
1	-6.493022	1.304628	2.961402
8	-2.699091	0.224397	0.445092
50	-1.654749	-0.239652	-1.438725
17	-1.448959	2.165613	-1.643952
17	-0.042285	-0.708735	-3.159637
17	-3.771953	-0.360707	-2.576058
17	-1.736961	-2.540184	-0.644791
6	-0.989588	-1.640645	3.982128
6	-0.677343	-1.748761	5.470277
6	-0.265605	-2.714459	3.179005
1	-2.072329	-1.793623	3.852528
1	-1.212408	-0.989502	6.053896
1	-0.972427	-2.734622	5.845044
1	0.397288	-1.634680	5.665134
1	-0.535122	-2.701834	2.114705
1	0.825543	-2.619013	3.261509
1	-0.534670	-3.702927	3.566739

1-spt-κ^{2}*O,O'*

atomic number	X(Å)	Y(Å)	Z(Å)
8	-0.020659	0.126794	0.127418
6	0.001598	0.070910	1.356412
8	1.136122	0.023232	2.003287
6	0.903898	0.080549	3.433347
6	-0.568457	-0.278823	3.602342
1	1.590177	-0.625043	3.903983
1	1.133549	1.098277	3.756351
1	-1.020119	0.388975	4.337232
7	-1.069257	0.053525	2.233227
6	-2.396386	0.069552	1.841427
6	-3.454261	0.269199	2.820062
6	-3.414468	1.163906	3.821345
1	-4.383440	-0.238545	2.564132
1	-2.507969	1.746112	3.994492
6	-4.567255	1.469569	4.698730
1	-4.838140	2.529108	4.614053
1	-5.440516	0.857186	4.457042
1	-4.293044	1.307617	5.748874
8	-2.732531	-0.083502	0.650971
50	-1.701640	-0.260369	-1.316470
17	-1.890583	2.156375	-1.343826
17	-0.121835	-0.352858	-3.123056
17	-3.823924	-0.633141	-2.382449
17	-1.398748	-2.582152	-0.676353
6	-0.868779	-1.731562	3.979431
6	-0.446362	-1.970906	5.423962
6	-0.243278	-2.752718	3.038498
1	-1.964113	-1.836791	3.927078
1	-0.904378	-1.245225	6.107061
1	-0.750159	-2.974071	5.741420
1	0.643818	-1.909634	5.540822
1	-0.585659	-2.638238	2.001857
1	0.853699	-2.697458	3.049621
1	-0.519944	-3.762901	3.358940

1-apc-κ*O*

atomic number	X(Å)	Y(Å)	Z(Å)
8	0.027294	-0.032593	0.045035
6	-0.011578	-0.010689	1.274683
8	1.089389	-0.010320	1.980682
6	0.781384	0.154702	3.389009
6	-0.694906	-0.213824	3.505867
1	1.450556	-0.500425	3.948372
1	0.980989	1.198280	3.641830
1	-1.199613	0.512458	4.150898
7	-1.122768	0.003328	2.097818
6	-2.426086	0.157326	1.663949
6	-3.468589	0.261985	2.660101
6	-4.761460	0.298102	2.279418
1	-3.205884	0.308420	3.712903
1	-4.987431	0.234044	1.213769
6	-5.900805	0.414523	3.209742
1	-6.578084	-0.439135	3.080286
1	-5.584730	0.471248	4.255214
1	-6.493022	1.304628	2.961402
8	-2.699091	0.224397	0.445092
50	-1.654749	-0.239652	-1.438725
17	-1.448959	2.165613	-1.643952
17	-0.042285	-0.708735	-3.159637
17	-3.771953	-0.360707	-2.576058
17	-1.736961	-2.540184	-0.644791
6	-0.989588	-1.640645	3.982128
6	-0.677343	-1.748761	5.470277
6	-0.265605	-2.714459	3.179005
1	-2.072329	-1.793623	3.852528
1	-1.212408	-0.989502	6.053896
1	-0.972427	-2.734622	5.845044
1	0.397288	-1.634680	5.665134
1	-0.535122	-2.701834	2.114705
1	0.825543	-2.619013	3.261509
1	-0.534670	-3.702927	3.566739

1-apc-κ*O'*

atomic number	X(Å)	Y(Å)	Z(Å)
8	3.982120	1.693712	0.440434
6	3.478950	0.605581	0.560742
8	4.112719	-0.453490	1.055556
6	3.222689	-1.584016	1.173141
6	2.051712	-1.261853	0.247927
1	3.782739	-2.474115	0.880646
1	2.920371	-1.663529	2.220845
1	1.102537	-1.517485	0.732420
7	2.175449	0.209871	0.192852
6	1.159724	1.025140	-0.214775
6	1.293392	2.464693	-0.136029
6	0.485767	3.259755	-0.863328
1	2.075788	2.882204	0.489483
1	-0.237626	2.794508	-1.533837
6	0.526025	4.736712	-0.837817
1	-0.461341	5.128241	-0.559586
1	1.274914	5.119629	-0.138745
1	0.734140	5.129595	-1.840929
8	0.113558	0.456748	-0.635934
6	2.102752	-1.916723	-1.138062
6	1.887089	-3.419980	-1.004355
6	3.379992	-1.609764	-1.909916
1	1.250644	-1.503730	-1.695670
1	0.970467	-3.652813	-0.447839
1	1.801868	-3.875289	-1.997352
1	2.728950	-3.908072	-0.495035
1	3.538357	-0.532651	-2.045860
1	4.266794	-2.028213	-1.414497
1	3.325011	-2.059677	-2.907542
17	-1.684822	-2.004999	-0.878954
50	-1.936703	0.084823	0.189266
17	-0.903880	0.571610	2.270372
17	-4.082694	-0.440633	1.192878
17	-2.743987	1.827098	-1.179465

1-apt-*κO’*

atomic number	X(Å)	Y(Å)	Z(Å)
8	0.066644	-0.683066	-0.060650
6	0.125793	-0.466283	1.121373
8	1.254944	-0.485518	1.825813
6	1.014255	-0.122915	3.204209
6	-0.475280	-0.372619	3.412909
1	1.662443	-0.745024	3.824384
1	1.284700	0.929637	3.326142
1	-0.925253	0.421499	4.021650
7	-0.937954	-0.203851	2.015809
6	-2.239771	0.064659	1.720036
6	-2.687013	0.536583	0.424594
6	-1.998521	1.400633	-0.339521
1	-3.711315	0.261172	0.174308
1	-1.007826	1.726574	-0.020704
6	-2.515139	1.988650	-1.594206
1	-1.842267	1.738765	-2.424636
1	-3.522215	1.633057	-1.830121
1	-2.524680	3.083520	-1.527468
8	-3.054242	-0.079858	2.672189
6	-0.840255	-1.736675	4.014340
6	-0.461492	-1.755706	5.490871
6	-0.235020	-2.919600	3.269153
1	-1.934361	-1.811302	3.947870
1	-0.924073	-0.923547	6.036185
1	-0.799250	-2.690129	5.952627
1	0.625971	-1.695679	5.634389
1	-0.538583	-2.950631	2.215162
1	0.862570	-2.913164	3.311242
1	-0.572739	-3.854043	3.730849
17	-4.321848	-0.178068	5.414780
50	-4.733511	1.121651	3.487299
17	-3.273422	2.961922	3.136639
17	-6.514616	2.455744	4.447156
17	-6.070239	0.194828	1.770010

1-apt-1*κO’*,2*κO’*

atomic number	X(Å)	Y(Å)	Z(Å)
8	-1.981312	-0.100954	0.004803
6	-1.192364	0.802565	0.274632
8	-1.546945	1.921778	0.851546
6	-0.372443	2.741211	1.113703
6	0.705842	2.165339	0.200152
1	-0.644936	3.773178	0.887541
1	-0.139780	2.635398	2.175613
1	1.659779	2.085257	0.732634
7	0.158738	0.801010	-0.003750
6	0.911428	-0.242564	-0.505907
6	0.336926	-1.561432	-0.640132
6	0.874183	-2.442455	-1.507510
1	-0.554663	-1.811455	-0.073837
1	1.727078	-2.128961	-2.110956
6	0.361132	-3.809874	-1.724936
1	1.162664	-4.539198	-1.547368
1	-0.490229	-4.042187	-1.078637
1	0.065045	-3.939906	-2.773625
8	2.096789	0.034589	-0.807294
50	-4.285025	-0.324427	0.122455
17	-3.974419	-0.001885	2.435963
17	-6.674204	-0.604018	0.166155
17	-3.720611	-2.450810	-0.721095
17	-4.239029	1.498627	-1.375824
6	0.910366	2.909203	-1.125350
6	1.557712	4.262095	-0.854190
6	-0.369357	3.056068	-1.939244
1	1.621321	2.302745	-1.703611
1	2.489236	4.158153	-0.284159
1	1.794847	4.759159	-1.801149
1	0.887360	4.929285	-0.295665
1	-0.826604	2.087817	-2.181174
1	-1.118086	3.672480	-1.422578
1	-0.144662	3.551940	-2.889802
17	4.605528	1.762413	-0.624590
50	4.129422	-0.407470	0.161320
17	2.797349	-0.716284	2.095385
17	6.235029	-0.753340	1.291321
17	4.359981	-2.169560	-1.384068

$SnCl_4$

atomic number	X(Å)	Y(Å)	Z(Å)
50	0.000000	0.000000	0.000000
17	1.348022	1.348022	1.348022
17	-1.348022	-1.348022	1.348022
17	-1.348022	1.348022	-1.348022
17	1.348022	-1.348022	-1.348022

1-apc

atomic number	X(Å)	Y(Å)	Z(Å)
8	-1.383758	2.067272	-0.262258
6	-2.145739	1.052525	-0.946442
6	-1.398985	-0.248909	-0.673670
7	-0.069757	0.278229	-0.322129
6	-0.147175	1.627645	0.008462
6	1.054985	-0.556379	-0.379767
8	0.890691	-1.709568	-0.765423
6	2.357837	-0.007284	0.013807
6	3.448611	-0.787944	-0.020110
6	4.810053	-0.343933	0.362306
6	-1.990755	-1.128676	0.434563
6	-2.188541	-0.391864	1.753277
6	-3.290864	-1.758623	-0.049196
8	0.703834	2.347749	0.478350
1	-2.168483	1.310770	-2.009108
1	-3.161451	1.072005	-0.544836
1	-1.308878	-0.845361	-1.588144
1	2.415934	1.027266	0.336717
1	3.334083	-1.822918	-0.346846
1	4.828717	0.707193	0.666144
1	5.508586	-0.485226	-0.471996
1	5.193884	-0.957883	1.186972
1	-1.260325	-1.934663	0.595022
1	-2.557268	-1.087777	2.515449
1	-2.931496	0.412400	1.663317
1	-1.255054	0.042600	2.131675
1	-3.681158	-2.454078	0.702281
1	-3.145847	-2.315525	-0.982923
1	-4.065641	-0.999381	-0.223548

H. Additional computations

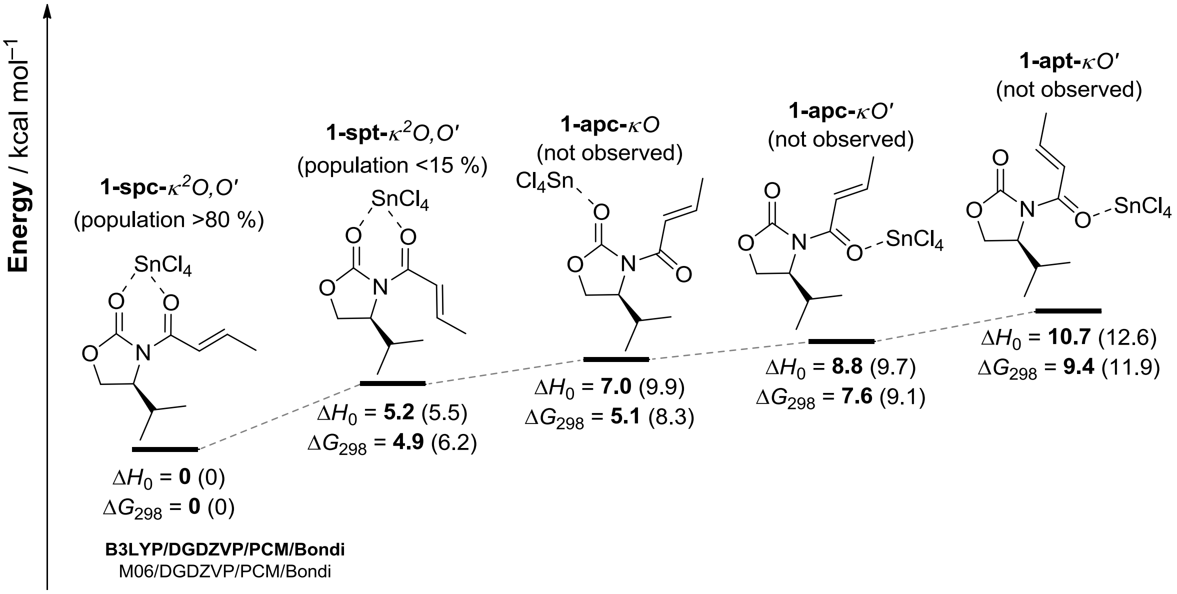


Fig. S6 Complex species of **1·SnCl$_4$**, computed at the B3LYP/DGDZVP/PCM/Bondi and M06/DGDZVP/PCM/Bondi level of theory. The population was determined before (*cf.* Chapter D).

Additional computations have been carried out using the DGDZVP[2] full electron basis set optimized for density functional methods to compare with our 6-31+G(*d,p*)/SDD split basis set that uses effective core potentials on the Sn atoms. All three approaches (M06/DGDZVP, B3LYP/DGDZVP, M06/6-31+G(*d,p*)/SDD) predict basically the same order of energies for the complex species (Fig. S5 and S6). Only the **1-apc-**κ*O′* is slightly above **1-apc-**κ*O*, when DGDZVP is used and slightly below with 6-31+G(*d,p*)/SDD. Most importantly, in agreement with the experiment all three approaches predict **1-spc-**κ²*O,O′* to be lowest and **1-spt-**κ²*O,O′* to be second in energy.

Agreement of computations with experiment for vibrational transition dipoles and vibrational frequencies is very good for the M06 approach, with the 6+31G(*d,p*)/SDD basis set performing somewhat better than the DGDZVP basis set (tables S16 and S17).[3] Agreement for the B3LYP computations is not as good. This survey justifies the usage of our split basis set for the underlying computations.

Table S12 Summary of the DFT computations (M06/DGDZVP/PCM/Bondi) for **1-apc** and SnCl$_4$.

	Energy	ZPVE	E+ZPVE	G_{298}
	(–au)	(au)	(–au)	(–au)
1-apc	670.2126714	0.2436358	669.9690356	670.010455
SnCl$_4$	7865.2395788	0.0045835	7865.2349953	7865.268696

Table S13 Summary of the DFT computations (M06/DGDZVP/PCM/Bondi) for the various tin complexes of **1**.

	Energy	ZPVE	E+ZPVE	ΔH_0	D_0	G_{298}	ΔG_{298}	D_{298}
Complex	(–au)	(au)	(–au)	(kcal mol^{-1})	(kcal mol^{-1})	(–au)	(kcal mol^{-1})	(kcal mol^{-1})
1-spc-κ²*O,O′*	8535.4932478	0.2504241	8535.2428237	0.0	24.3	8535.297857	0.0	11.7
1-spt-κ²*O,O′*	8535.4845380	0.2505506	8535.2339874	5.5	18.8	8535.287958	6.2	5.5
1-apc-κ*O*	8535.4764862	0.2494589	8535.2270273	9.9	14.4	8535.284656	8.3	3.5
1-apc-κ*O′*	8535.4773898	0.2500385	8535.2273513	9.7	14.6	8535.283302	9.1	2.6
1-apt-κ*O'*	8535.4725351	0.2498188	8535.2227163	12.6	11.7	8535.278925	11.9	–0.1
1-apc-1κ*O*,2κ*O′*	16400.7369975	0.2567700	16400.4802275	–	25.9	16400.550526	–	1.7

Table S14 Summary of the DFT computations (B3LYP/DGDZVP/PCM/Bondi) for the **1-apc** and $SnCl_4$.

	Energy (–au)	**ZPVE** (au)	**E+ZPVE** (–au)	G_{298} (–au)
1-apc	670.6440066	0.2430218	670.4009848	670.443013
$SnCl_4$	7865.6029564	0.0044256	7865.5985308	7865.632356

Table S15 Summary of the DFT computations (B3LYP/DGDZVP/PCM/Bondi) for the various tin complexes of **1**.

Complex	**Energy** (–au)	**ZPVE** (au)	**E+ZPVE** (–au)	ΔH_0 (kcal mol^{-1})	D_0 (kcal mol^{-1})	G_{298} (–au)	ΔG_{298} (kcal mol^{-1})	D_{298} (kcal mol^{-1})
1-spc-κ^2O,O'	8536.2726498	0.2500566	8536.0225932	0.0	14.5	8536.078344	0.0	1.9
1-spt-κ^2O,O'	8536.2638513	0.2496040	8536.0142473	5.2	9.2	8536.070598	4.9	−3.0
1-apc-κO	8536.2601734	0.2487349	8536.0114385	7.0	7.5	8536.070219	5.1	−3.2
1-apc-$\kappa O'$	8536.2577467	0.2491746	8536.0085721	8.8	5.7	8536.066249	7.6	−5.7
1-apt-$\kappa O'$	8536.2544542	0.2488564	8536.0055978	10.7	3.8	8536.063415	9.4	−7.5
1-apc-1κO,2$\kappa O'$	16401.8694725	0.2546079	16401.6148646	–	10.6	16401.690077	–	−11.1

Table S16 Comparison of measured and computed vibrational frequencies and transition dipole angles for free **1**. All computations use SCRF with PCM/Bondi. Vibrational frequencies have been scaled by a uniform factor of 0.9689, 0.9695, 0.9932 for M06/6-31+G(*d*,*p*)/SDD, M06/DGDZVP, B3LYP/DGDZVP, respectively. The factor is chosen such, that optimal agreement is achieved for **1** and **1-spc**-κ^2O,O'. Transition dipole angles are given as determined by the anisotropy method as well as by the annihilation method (value in brackets).

	experiment	**M06/6-31+G(*d*,*p*)/SDD**	**M06/DGDZVP**	**B3LYP/DGDZVP**
ν_1 (cm^{-1})	1638	1642	1648	1647
ν_2 (cm^{-1})	1686	1687	1670	1697
ν_3 (cm^{-1})	1777	1774	1777	1764
ν_1/ν_2 (°)	57 (60)	64	62	69
ν_1/ν_3 (°)	27 (30)	21	18	1
ν_2/ν_3 (°)	43 (46)	43	45	68

Table S17 Comparison of measured and computed vibrational frequencies and transition dipole angles for the major complex **1-spc**-κ^2O,O'. All computations use SCRF with PCM/Bondi. Vibrational frequencies have been scaled by a uniform factor of 0.9689, 0.9695, 0.9932 for M06/6-31+G(*d*,*p*)/SDD, M06/DGDZVP, B3LYP/DGDZVP, respectively. The factor is chosen such, that optimal agreement is achieved for **1** and **1-spc**-κ^2O,O'. Transition dipole angles are given as determined by the anisotropy method as well as by the annihilation method (value in brackets).

	experiment	**M06/6-31+G(*d*,*p*)/SDD**	**M06/DGDZVP**	**B3LYP/DGDZVP**
ν'_1 (cm^{-1})	1567	1567	1562	1554
ν'_2 (cm^{-1})	1633	1634	1639	1653
ν'_3 (cm^{-1})	1727	1725	1714	1713
ν'_1/ν'_2 (°)	18 (15)	16	5	10
ν'_1/ν'_3 (°)	46 (46)	46	48	53
ν'_2/ν'_3 (°)	48 (49)	61	52	43

Cartesian Coordinates

B3LYP/DGDZVP/PCM/BONDI

1-spc-κ^2O,O'

atomic number	X(Å)	Y(Å)	Z(Å)
8	-0.193031	-1.544905	-0.662612
6	1.032499	-1.396187	-0.780932
8	1.790218	-2.413244	-1.134735
6	3.166726	-1.962538	-1.351385
6	3.246828	-0.591431	-0.657452
1	3.819501	-2.718406	-0.922361
1	3.313502	-1.900022	-2.429848
1	3.737395	0.113832	-1.328302
7	1.787935	-0.250420	-0.583141
6	1.253592	1.017407	-0.401584
6	2.163104	2.153704	-0.377924
6	1.699587	3.397983	-0.118288
1	3.215180	1.995645	-0.577735
1	0.637702	3.523379	0.085456
6	2.542489	4.625062	-0.085579
1	2.456582	5.104387	0.897679
1	3.593988	4.421166	-0.299028
1	2.158715	5.352883	-0.811684
8	0.011839	1.194536	-0.280677
50	-1.753125	-0.100040	0.077013
17	-2.218815	0.252734	-2.297299
17	-3.324455	-1.930845	0.291209
17	-3.043711	1.823702	0.791796
17	-0.768203	-0.471136	2.292148
6	3.942722	-0.573522	0.724128
6	5.460163	-0.744943	0.536681
6	3.378178	-1.593111	1.726634
1	3.775711	0.426772	1.139854
1	5.871195	0.007775	-0.145126
1	5.964912	-0.637207	1.501542
1	5.712749	-1.736141	0.143679
1	2.307369	-1.452830	1.903140
1	3.541827	-2.626086	1.399978
1	3.884970	-1.471581	2.688974

1-apc-κO

atomic number	X(Å)	Y(Å)	Z(Å)
8	-0.106925	0.379138	0.002013
6	-1.087277	-0.338235	0.309107
8	-0.936481	-1.619549	0.597880
6	-2.211207	-2.173088	1.067955
6	-3.264803	-1.129682	0.656633
1	-2.328174	-3.144156	0.592812
1	-2.123227	-2.288998	2.148575
1	-3.904490	-0.884097	1.504668
7	-2.392461	0.049799	0.384714
6	-2.954103	1.363405	0.359848
6	-2.100003	2.497383	-0.031136
6	-2.600946	3.749485	-0.018441
1	-1.078965	2.310149	-0.334866
1	-3.633693	3.891771	0.297541
6	-1.842223	4.975176	-0.411495
1	-1.820270	5.686474	0.423659
1	-0.817313	4.751049	-0.716323
1	-2.357574	5.485101	-1.235305
8	-4.141578	1.460798	0.661733
50	2.111017	-0.141485	-0.027584
17	1.859291	-0.615270	2.296056
17	4.495613	-0.616750	-0.075783
17	2.290798	2.146293	-0.658536
17	1.556163	-1.693387	-1.749519
6	-4.154832	-1.506223	-0.550506
6	-5.127712	-2.627752	-0.147015
6	-3.367348	-1.868685	-1.819321
1	-4.753209	-0.615974	-0.768012
1	-5.718284	-2.348876	0.732668
1	-5.822456	-2.831407	-0.968028
1	-4.602779	-3.563632	0.077698
1	-2.692294	-1.063229	-2.127223
1	-2.775547	-2.782178	-1.691400
1	-4.064455	-2.045218	-2.644777

1-spt-κ^2O,O'

atomic number	X(Å)	Y(Å)	Z(Å)
8	0.285977	-1.158049	1.073861
6	-0.951296	-1.079584	1.061919
8	-1.677886	-2.000710	1.658054
6	-3.093100	-1.623455	1.628439
6	-3.190396	-0.540038	0.541622
1	-3.657468	-2.527021	1.411835
1	-3.340438	-1.248437	2.621826
1	-3.797872	0.279396	0.912841
7	-1.752094	-0.103896	0.483116
6	-1.263731	1.024123	-0.154702
6	-2.148101	2.134500	-0.529558
6	-3.067419	2.704415	0.274069
1	-1.862017	2.608593	-1.465330
1	-3.269079	2.284809	1.258143
6	-3.818967	3.950455	-0.067923
1	-3.602542	4.731045	0.671480
1	-3.570750	4.323684	-1.063865
1	-4.897991	3.760441	-0.011203
8	-0.048798	1.145848	-0.450056
50	1.841793	0.008053	-0.063505
17	1.963596	1.369918	1.964684
17	3.542743	-1.549746	0.666339
17	3.074888	1.597108	-1.412706
17	1.169552	-1.356542	-1.982635
6	-3.731220	-0.994629	-0.832576
6	-5.247509	-1.234076	-0.724322
6	-3.003914	-2.209939	-1.427997
1	-3.582468	-0.146072	-1.510816
1	-5.769838	-0.344178	-0.356034
1	-5.654070	-1.479651	-1.709961
1	-5.482345	-2.068879	-0.054316
1	-1.932978	-2.029150	-1.562464
1	-3.127594	-3.105696	-0.809424
1	-3.421216	-2.434188	-2.414538

1-apc-$\kappa O'$

atomic number	X(Å)	Y(Å)	Z(Å)
8	-3.879397	2.246921	-0.541159
6	-3.595495	1.075095	-0.669472
8	-4.433305	0.168036	-1.193889
6	-3.773724	-1.124838	-1.335829
6	-2.565442	-1.056794	-0.389764
1	-4.501023	-1.889814	-1.072376
1	-3.479507	-1.230501	-2.381677
1	-1.681728	-1.478205	-0.868089
7	-2.393824	0.417704	-0.300984
6	-1.211800	1.000895	0.072522
6	-1.078317	2.452009	0.102428
6	-0.095793	3.053730	0.807230
1	-1.822289	3.039499	-0.418698
1	0.599861	2.444784	1.380646
6	0.096558	4.530936	0.892841
1	1.105244	4.790421	0.546911
1	-0.638419	5.084148	0.304033
1	0.039219	4.854730	1.939500
8	-0.275163	0.200233	0.391721
6	-2.756546	-1.724910	0.994222
6	-2.797454	-3.253915	0.831529
6	-3.975419	-1.208653	1.776490
1	-1.858062	-1.479898	1.569536
1	-1.910957	-3.625018	0.306397
1	-2.828564	-3.731041	1.816235
1	-3.685134	-3.582939	0.279164
1	-3.931926	-0.126959	1.942309
1	-4.919658	-1.440320	1.270883
1	-4.005835	-1.687065	2.760807
17	1.072798	-2.529437	-0.361035
50	1.860475	-0.302434	-0.073849
17	1.655563	1.163533	-1.948704
17	4.196735	-0.821912	-0.537566
17	2.279334	0.356821	2.181258

1-apt-$\kappa O'$

atomic number	X(Å)	Y(Å)	Z(Å)
8	-3.822888	1.954174	0.849145
6	-3.649236	0.976991	0.157335
8	-4.647605	0.298993	-0.431439
6	-4.120796	-0.785757	-1.252586
6	-2.712950	-1.041671	-0.696023
1	-4.800338	-1.628944	-1.148729
1	-4.103949	-0.440586	-2.288231
1	-2.008065	-1.231662	-1.506640
7	-2.427439	0.312677	-0.143193
6	-1.157498	0.750859	0.102163
6	-0.823852	2.147620	0.372172
6	-1.383788	3.204527	-0.247889
1	0.030795	2.286427	1.028430
1	-2.197618	3.048836	-0.952934
6	-0.940334	4.617873	-0.062106
1	-1.787244	5.224606	0.282458
1	-0.120808	4.705240	0.654756
1	-0.625482	5.042369	-1.023258
8	-0.252224	-0.141973	0.049008
6	-2.603635	-2.181874	0.345099
6	-2.773825	-3.537409	-0.362467
6	-3.563285	-2.043952	1.538617
1	-1.580697	-2.139832	0.729008
1	-2.063647	-3.648515	-1.189329
1	-2.593871	-4.351790	0.346350
1	-3.786124	-3.666718	-0.762170
1	-3.413318	-1.106341	2.084483
1	-4.614542	-2.098934	1.234559
1	-3.383898	-2.860827	2.245200
17	1.610278	-2.525987	-0.386158
50	1.989474	-0.207679	-0.004556
17	1.842463	1.245891	-1.896553
17	4.421941	-0.341750	-0.078673
17	1.932617	0.535320	2.267068

1-apt-1$\kappa O'$,2$\kappa O'$

atomic number	X(Å)	Y(Å)	Z(Å)
8	2.096136	-0.051191	0.164365
6	1.348662	0.886664	-0.160306
8	1.800965	2.001273	-0.696485
6	0.678267	2.865068	-1.084904
6	-0.520055	2.312974	-0.298418
1	0.958102	3.881917	-0.821737
1	0.564510	2.765912	-2.164682
1	-1.393856	2.231496	-0.943809
7	-0.026430	0.930647	-0.008916
6	-0.889130	-0.104346	0.339242
6	-0.367935	-1.436600	0.603878
6	-1.074103	-2.333787	1.327526
1	0.625666	-1.678088	0.252428
1	-2.041069	-2.047196	1.735086
6	-0.603196	-3.710003	1.653437
1	-1.331712	-4.442258	1.282315
1	0.378296	-3.929629	1.228376
1	-0.565573	-3.842125	2.741881
8	-2.106353	0.216341	0.405057
50	4.390915	-0.368110	-0.120770
17	3.887121	-0.188619	-2.440370
17	6.760202	-0.779244	-0.400233
17	3.862064	-2.423361	0.944603
17	4.622518	1.543714	1.274246
6	-0.898740	3.096025	0.981273
6	-1.498675	4.458110	0.591948
6	0.257724	3.254139	1.981511
1	-1.689418	2.514816	1.465642
1	-2.335865	4.343371	-0.104585
1	-1.872276	4.965455	1.486739
1	-0.754528	5.115995	0.128562
1	0.654204	2.288066	2.311303
1	1.084997	3.841186	1.566954
1	-0.101205	3.779237	2.872284
17	-4.360399	1.856118	-0.988815
50	-4.251746	-0.380628	-0.193442
17	-3.236215	-1.971351	-1.643993
17	-6.529960	-0.989665	-0.769316
17	-4.527484	-0.690336	2.149857

$SnCl_4$

atomic number	X(Å)	Y(Å)	Z(Å)
50	0.000000	0.000000	0.000000
17	1.358564	1.358564	1.358564
17	-1.358564	-1.358564	1.358564
17	-1.358564	1.358564	-1.358564
17	1.358564	-1.358564	-1.358564

1-apc

atomic number	X(Å)	Y(Å)	Z(Å)
8	-1.362655	2.103178	-0.270277
6	-2.139530	1.081267	-0.956741
6	-1.406079	-0.237656	-0.664913
7	-0.067227	0.277542	-0.292481
6	-0.124651	1.639693	0.013487
6	1.059646	-0.562874	-0.362914
8	0.890552	-1.720916	-0.759543
6	2.378993	-0.024005	0.032137
6	3.475005	-0.805214	-0.024280
6	4.854722	-0.367704	0.355118
6	-2.036971	-1.127892	0.433162
6	-2.268332	-0.400516	1.767662
6	-3.331838	-1.769102	-0.093665
8	0.740753	2.362212	0.475575
1	-2.145244	1.329212	-2.020436
1	-3.153575	1.121387	-0.562381
1	-1.306478	-0.827857	-1.577042
1	2.441252	1.001916	0.370783
1	3.363440	-1.833181	-0.367416
1	4.883693	0.673689	0.685603
1	5.537006	-0.490105	-0.495565
1	5.245502	-1.006309	1.157420
1	-1.318307	-1.934830	0.609683
1	-2.648175	-1.108007	2.512333
1	-3.006321	0.404629	1.674949
1	-1.342949	0.028988	2.165857
1	-3.738100	-2.463284	0.649235
1	-3.151300	-2.331763	-1.016574
1	-4.104846	-1.019036	-0.299442

Cartesian Coordinates

M06/DGDZVP/PCM/BONDI

1-spc-κ^2O,O'

atomic number	X(Å)	Y(Å)	Z(Å)
8	-0.208855	-1.558022	-0.663062
6	1.009133	-1.416772	-0.788271
8	1.767182	-2.441227	-1.083844
6	3.129673	-2.002707	-1.307379
6	3.206752	-0.617989	-0.671894
1	3.788961	-2.738832	-0.849380
1	3.287764	-1.982020	-2.385973
1	3.731415	0.057924	-1.351512
7	1.762781	-0.266155	-0.648568
6	1.243842	1.003011	-0.473617
6	2.163151	2.122292	-0.469337
6	1.726606	3.347458	-0.115795
1	3.201022	1.970055	-0.748436
1	0.681517	3.457874	0.173562
6	2.574376	4.557717	-0.082475
1	2.566728	4.988452	0.923912
1	3.603963	4.354097	-0.381813
1	2.149964	5.322280	-0.741456
8	0.014782	1.196760	-0.339719
50	-1.733915	-0.087279	0.077042
17	-2.231698	0.221887	-2.268972
17	-3.293128	-1.884276	0.358757
17	-2.963126	1.843319	0.791615
17	-0.684512	-0.434664	2.239166
6	3.835834	-0.556324	0.722979
6	5.340872	-0.767822	0.609369
6	3.211674	-1.525134	1.718931
1	3.667707	0.464436	1.094593
1	5.798739	-0.055947	-0.085549
1	5.811385	-0.637613	1.587816
1	5.578545	-1.781484	0.266026
1	2.135142	-1.360613	1.848980
1	3.370614	-2.569970	1.426558
1	3.678372	-1.390604	2.698849

1-apc-κO

atomic number	X(Å)	Y(Å)	Z(Å)
8	-0.123459	0.394618	0.184062
6	-1.094357	-0.322478	0.480659
8	-0.946281	-1.584574	0.817977
6	-2.229588	-2.127260	1.229596
6	-3.254639	-1.146841	0.671258
1	-2.300909	-3.133847	0.818528
1	-2.224330	-2.169592	2.319196
1	-4.018801	-0.917705	1.418932
7	-2.402350	0.047783	0.486545
6	-2.989500	1.333603	0.336315
6	-2.112268	2.481707	0.091515
6	-2.655009	3.694468	-0.106071
1	-1.036722	2.343499	0.061722
1	-3.741158	3.784247	-0.074742
6	-1.875407	4.927241	-0.373538
1	-2.084933	5.681194	0.392519
1	-0.800343	4.735493	-0.398536
1	-2.181455	5.367303	-1.328283
8	-4.205353	1.398746	0.430358
50	2.072350	-0.119826	-0.031253
17	2.023247	-0.607390	2.276929
17	4.413795	-0.597509	-0.302982
17	2.187937	2.155258	-0.634191
17	1.343233	-1.631553	-1.690696
6	-3.928069	-1.574450	-0.636637
6	-4.877562	-2.736230	-0.371445
6	-2.935517	-1.910304	-1.742982
1	-4.528597	-0.714998	-0.959568
1	-5.597597	-2.495361	0.417507
1	-5.438255	-2.978479	-1.278882
1	-4.335080	-3.641863	-0.073752
1	-2.267685	-1.072154	-1.974113
1	-2.317520	-2.780235	-1.486763
1	-3.474998	-2.157434	-2.662123

1-spt-κ^2O,O'

atomic number	X(Å)	Y(Å)	Z(Å)
8	0.294481	-1.086839	1.162965
6	-0.935727	-1.030962	1.123455
8	-1.659965	-1.964905	1.682620
6	-3.063252	-1.613118	1.616223
6	-3.149833	-0.540494	0.537257
1	-3.617371	-2.521668	1.383588
1	-3.349616	-1.245203	2.601883
1	-3.813438	0.254714	0.875300
7	-1.735992	-0.061584	0.542329
6	-1.257361	1.048711	-0.126841
6	-2.162080	2.122089	-0.520932
6	-3.107937	2.651234	0.272187
1	-1.879111	2.610610	-1.451038
1	-3.298813	2.216382	1.253054
6	-3.895041	3.859243	-0.074226
1	-3.730809	4.641847	0.672970
1	-3.636385	4.246784	-1.061010
1	-4.964650	3.626666	-0.047070
8	-0.052381	1.180970	-0.421572
50	1.815399	0.021217	-0.063973
17	2.011504	1.425442	1.896326
17	3.491551	-1.530853	0.648605
17	3.007275	1.526152	-1.497171
17	1.034500	-1.375498	-1.883758
6	-3.584395	-1.014819	-0.850067
6	-5.066300	-1.367304	-0.819127
6	-2.748623	-2.166889	-1.390775
1	-3.458821	-0.151510	-1.519620
1	-5.672394	-0.535171	-0.445768
1	-5.412016	-1.614119	-1.826568
1	-5.259048	-2.241170	-0.185735
1	-1.686694	-1.907813	-1.480689
1	-2.833884	-3.060285	-0.760365
1	-3.100828	-2.438926	-2.389672

1-apc-$\kappa O'$

atomic number	X(Å)	Y(Å)	Z(Å)
8	3.773669	2.134545	0.689682
6	3.451880	0.976176	0.758743
8	4.218495	0.019162	1.278127
6	3.514987	-1.239104	1.317901
6	2.366301	-1.086961	0.324678
1	4.225105	-2.021417	1.049176
1	3.164053	-1.393861	2.339944
1	1.442384	-1.500781	0.743057
7	2.255172	0.383037	0.296635
6	1.151608	1.033047	-0.163281
6	1.046737	2.475581	-0.061837
6	0.226100	3.150610	-0.888998
1	1.670292	2.997585	0.655917
1	-0.320849	2.592912	-1.648884
6	0.034773	4.618032	-0.864572
1	-1.029178	4.846937	-0.738773
1	0.603110	5.096465	-0.064963
1	0.329118	5.051986	-1.825578
8	0.236726	0.314471	-0.663348
6	2.607217	-1.688163	-1.064062
6	2.624597	-3.208929	-0.970971
6	3.866244	-1.160898	-1.740376
1	1.740344	-1.398506	-1.672507
1	1.723675	-3.595408	-0.481628
1	2.677334	-3.644475	-1.973030
1	3.496650	-3.570651	-0.413012
1	3.855654	-0.070004	-1.844155
1	4.772484	-1.445156	-1.191577
1	3.950156	-1.584355	-2.745644
17	-1.223557	-2.348227	-0.961836
50	-1.789531	-0.302994	0.065046
17	-0.948070	0.284212	2.202211
17	-3.899529	-1.079328	0.937748
17	-2.739656	1.328366	-1.344953

1-apt-*κO’*

atomic number	X(Å)	Y(Å)	Z(Å)
8	3.883729	1.936720	-0.618251
6	3.586495	0.942775	-0.010013
8	4.449284	0.212301	0.696461
6	3.772202	-0.869523	1.371476
6	2.478004	-1.063978	0.591282
1	4.435611	-1.734392	1.354000
1	3.594179	-0.562392	2.404046
1	1.639595	-1.267833	1.267271
7	2.322300	0.306596	0.058675
6	1.122502	0.773440	-0.378436
6	0.850446	2.180692	-0.605615
6	1.311413	3.162305	0.187367
1	0.105226	2.382948	-1.373510
1	1.991159	2.911869	1.001558
6	0.926644	4.586086	0.056945
1	1.822342	5.193490	-0.110595
1	0.225590	4.746741	-0.763973
1	0.479782	4.945170	0.989249
8	0.222409	-0.098745	-0.539623
6	2.521290	-2.139780	-0.500312
6	2.510858	-3.519327	0.147190
6	3.688846	-1.986082	-1.466457
1	1.589063	-2.031652	-1.068449
1	1.646321	-3.643518	0.808713
1	2.459535	-4.294007	-0.623407
1	3.419749	-3.701184	0.733616
1	3.684210	-1.014752	-1.973847
1	4.655386	-2.104854	-0.961764
1	3.627696	-2.757111	-2.239961
17	-1.562211	-2.510262	-0.295734
50	-1.933110	-0.199639	-0.007975
17	-1.241408	0.736396	2.057727
17	-4.246599	-0.385766	0.634760
17	-2.363406	1.098772	-1.933470

1-apt-1*κO’*,2*κO’*

atomic number	X(Å)	Y(Å)	Z(Å)
8	2.096136	-0.051191	0.164365
6	1.348662	0.886664	-0.160306
8	1.800965	2.001273	-0.696485
6	0.678267	2.865068	-1.084904
6	-0.520055	2.312974	-0.298418
1	0.958102	3.881917	-0.821737
1	0.564510	2.765912	-2.164682
1	-1.393856	2.231496	-0.943809
7	-0.026430	0.930647	-0.008916
6	-0.889130	-0.104346	0.339242
6	-0.367935	-1.436600	0.603878
6	-1.074103	-2.333787	1.327526
1	0.625666	-1.678088	0.252428
1	-2.041069	-2.047196	1.735086
6	-0.603196	-3.710003	1.653437
1	-1.331712	-4.442258	1.282315
1	0.378296	-3.929629	1.228376
1	-0.565573	-3.842125	2.741881
8	-2.106353	0.216341	0.405057
50	4.390915	-0.368110	-0.120770
17	3.887121	-0.188619	-2.440370
17	6.760202	-0.779244	-0.400233
17	3.862064	-2.423361	0.944603
17	4.622518	1.543714	1.274246
6	-0.898740	3.096025	0.981273
6	-1.498675	4.458110	0.591948
6	0.257724	3.254139	1.981511
1	-1.689418	2.514816	1.465642
1	-2.335865	4.343371	-0.104585
1	-1.872276	4.965455	1.486739
1	-0.754528	5.115995	0.128562
1	0.654204	2.288066	2.311303
1	1.084997	3.841186	1.566954
1	-0.101205	3.779237	2.872284
17	-4.360399	1.856118	-0.988815
50	-4.251746	-0.380628	-0.193442
17	-3.236215	-1.971351	-1.643993
17	-6.529960	-0.989665	-0.769316
17	-4.527484	-0.690336	2.149857

$SnCl_4$

atomic number	X(Å)	Y(Å)	Z(Å)
50	0.000000	0.000000	0.000000
17	1.346196	1.346196	1.346196
17	-1.346196	-1.346196	1.346196
17	-1.346196	1.346196	-1.346196
17	1.346196	-1.346196	-1.346196

1-apc

atomic number	X(Å)	Y(Å)	Z(Å)
8	-1.390732	2.068824	-0.255321
6	-2.147665	1.053037	-0.939341
6	-1.398667	-0.247776	-0.673369
7	-0.072782	0.278889	-0.319758
6	-0.149847	1.630026	0.008409
6	1.052433	-0.554021	-0.381364
8	0.893389	-1.707523	-0.769797
6	2.357033	-0.003616	0.015688
6	3.446742	-0.786043	-0.022003
6	4.811514	-0.346887	0.363720
6	-1.986711	-1.132750	0.431082
6	-2.181463	-0.399929	1.752368
6	-3.288336	-1.761253	-0.049679
8	0.703466	2.353010	0.471091
1	-2.173745	1.311094	-2.000504
1	-3.162425	1.066519	-0.538529
1	-1.310518	-0.838133	-1.590634
1	2.419156	1.028701	0.343440
1	3.328022	-1.817894	-0.354207
1	4.831804	0.700032	0.674469
1	5.506363	-0.483109	-0.471555
1	5.190999	-0.966926	1.182792
1	-1.257104	-1.938030	0.587618
1	-2.550888	-1.095804	2.512134
1	-2.920751	0.406131	1.665378
1	-1.246956	0.030094	2.129710
1	-3.674054	-2.459226	0.699634
1	-3.146744	-2.312517	-0.985388
1	-4.062859	-1.002362	-0.216893

Notes and references

[a] *Institute of Biophysics, Johann Wolfgang Goethe-University, Max-von-Laue-Str. 1, 60438 Frankfurt, Germany. Fax: +49 69 794 46421; Tel: +49 69 794 46410; E-mail: bredenbeck@biophysik.uni-frankfurt.de*
[b] *Institute of Organic Chemistry, Justus-Liebig University, Heinrich-Buff-Ring 58, 35392 Giessen, Germany. Fax: +49 641 99 34304; Tel: +49 641 99 34301; E-mail: prs@org.chemie.uni-giessen.de*
[c] *CEF-MC, Johann Wolfgang Goethe-University, Max-von-Laue-Str. 9, 60438 Frankfurt, Germany.*

1. A. T. Messmer, K. M. Lippert, S. Steinwand, E.-B. W. Lerch, K. Hof, D. Ley, D. Gerbig, H. Hausmann, P. R. Schreiner, and J. Bredenbeck, *Chem. Eur. J.*, 2012, **18**, 14989–14995.
2. N. Godbout, D. R. Salahub, J. Andzelm, and E. Wimmer, *Can. J. Chem.*, 1992, **70**, 560–571.
3. A detailed study of the basis set dependence of transition dipole angles for 1 can be found in ref. 1.