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p-Block Metal Complexes with Bis(pyrazol-1-yl)acetato Ligands

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Table S1. Crystal data and refinement details of complexes **1b** and **2**.

	$[Sn_2(bpza)_4]$ (1b)	**$[Sn(bdmpza)_2]$ (2)**
CCDC number	2117083	2117084
Empirical formula	$2 \times C_{32}H_{28}N_{16}O_8Sn_2$	$C_{24}H_{30}N_8O_4Sn$
Formula mass	2004.16	613.25
Crystal color/habit	colourless block	colourless block
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$C2/c$
a [Å]	11.0397(3)	8.2234(3)
b [Å]	14.1993(5)	22.7396(7)
c [Å]	24.7702(8)	14.1698(5)
α [°]	90	90
β [°]	90.993(3)	99.184(3)
γ [°]	90	90
V [Å^3]	3882.3(2)	2615.73(15)
θ [°]	2.182 - 29.831	2.912 - 26.040
h	−15 to 15	−9 to 10
k	−19 to 19	−25 to 28
l	−34 to 33	−17 to 17
F(000)	1984	1248
Z	2	4
μ (Mo-K_α) [mm^{-1}]	1.358	1.023
Crystal size [mm]	0.278 × 0.141 × 0.059	0.2565 × 0.1645 × 0.1024
D_{calc} [g cm^{-3}], T [K]	1.714, 100.00(10)	1.557, 100.0(2)
Reflections collected	38593	7893
Independent reflections	18098	2586
Observed reflections ($I > 2\sigma I$)	15800	2466
Parameter	1092	172
Weight parameter a, b	0.0274/0.8504	0.0176/3.1448
R_1 (observed)	0.0343	0.0227
R_1 (overall)	0.0428	0.0245
ωR_2 (observed)	0.0694	0.0511
ωR_2 (overall)	0.0739	0.0522
Diff. peak/hole [e Å^{-3}]	−0.920/1.036	−0.335/0.347
Goodness-of-fit on F^2	1.023	1.036
Flack parameter	0.43(2)	-

Table S2. Crystal data and refinement details of complexes **3**, **4** and **5**.

	[Sn(bdmpza)F_3] (3)	**[Ga(bdmpza)$_2$]ClO_4 (4)**	**[Ga(bpza)$_2$][$GaCl_4$] (5)**
CCDC number	2117085	2117086	2117087
Empirical formula	$C_{12}H_{15}F_3N_4O_2Sn$	$C_{24}H_{30}GaN_8O_4$, ClO_4 × CH_2Cl_2	$C_{16}H_{14}GaN_8O_4$, $GaCl_4$
Formula mass	422.97	748.65	663.59
Crystal color/habit	colourless block	colourless block	colourless block
Crystal system	triclinic	triclinic	monoclinic
Space group	*P*–1	*P*–1	*C2/c*
a [Å]	8.1077(4)	9.7565(5)	17.0141(5)
b [Å]	8.4826(5)	12.3535(6)	8.3409(3)
c [Å]	11.9826(6)	14.4351(7)	16.4275(6)
α [°]	110.060(5)	101.090(4)	90
β [°]	98.633(4)	103.231(4)	91.304(3)
γ [°]	106.314(5)	106.077(4)	90
V [Å^3]	714.63(7)	1565.38(14)	2330.68(14)
θ [°]	3.093 - 29.763	3.014 - 29.608	5.201 - 72.804
h	−10 to 10	−13 to 12	−20 to 20
k	−11 to 11	−16 to 17	−10 to 9
l	−16 to 16	−19 to 19	−16 to 19
F(000)	416	768	1312
Z	2	2	4
μ (Mo-K_α) [mm^{-1}]	1.835	1.196	-
μ (Cu-K_α) [mm^{-1}]	-	-	7.446
Crystal size [mm]	0.0874 × 0.0716 × 0.0529	0.4462 × 0.1945 × 0.0672	0.343 × 0.184 × 0.049
D_{calc} [g cm^{-3}], *T* [K]	1.966, 100.00(10)	1.588, 100.01(10)	1.891, 99.99(10)
Reflections collected	9668	17048	6667
Independent reflections	3505	7502	2241
Observed reflections ($I > 2\sigma I$)	3226	6546	2075
Parameter	203	424	156
Weight parameter *a*, *b*	0.0150/0.2722	0.0276/1.0502	0.0377/ 4.4192
R_1 (observed)	0.0277	0.0343	0.0293
R_1 (overall)	0.0313	0.0413	0.0320
ωR_2 (observed)	0.0505	0.0766	0.0739
ωR_2 (overall)	0.0520	0.0799	0.0762
Diff. peak/hole [e Å^{-3}]	−0.765/0.665	−0.603/0.441	−0.596/0.733
Goodness-of-fit on F^2	1.075	1.036	1.079

Table S3. Selected distances and angles of $[Sn_2(bpza)_4]$ (**1b**).

1st molecule		**2nd molecule**	
Distance (Å)			
Sn1-N11	2.394(4)	Sn3-N111	2.412(4)
Sn1-N21	2.832(7)	Sn3-N121	2.814(6)
Sn1-N51	2.558(5)	Sn3-N151	2.539(5)
Sn1-O1	2.131(4)	Sn3-O101	2.132(4)
Sn1-O3	2.193(5)	Sn3-O103	2.198(5)
Sn2-N71	2.823(7)	Sn4-N171	2.818(6)
Sn2-N81	2.396(4)	Sn4-N181	2.391(4)
Sn2-N41	2.557(5)	Sn4-N141	2.591(5)
Sn2-O5	2.209(5)	Sn4-O105	2.210(4)
Sn2-07	2.137(4)	Sn4-O107	2.145(5)
Angle (◦)			
N11-Sn1-O1	76.63(15)	N111-Sn3-O101	77.10(15)
N21-Sn1-O1	71.1(2)	N121-Sn3-O101	71.00(19)
N11-Sn1-O3	77.0(2)	N111-Sn3-O103	75.48(18)
N21-Sn1-N11	72.1(2)	N121-Sn3-N111	72.37(18)
N51-Sn1-O1	78.14(16)	N151-Sn3-O101	79.53(15)
N21-Sn1-N51	118.54(16)	N121-Sn3-N151	119.72(17)
N51-Sn1-O3	79.57(16)	N151-Sn3-O103	79.33(16)
O1-Sn1-O3	83.86(17)	O101-Sn3-O103	80.86(17)
N11-Sn1-N51	147.1(2)	N111-Sn3-N151	147.88(19)
N21-Sn1-O3	143.79(16)	N121-Sn3-O103	141.00(16)
N71-Sn2-O7	71.7(2)	N171-Sn4-O107	71.71(19)
N81-Sn2-O7	77.39(15)	N181-Sn4-O107	76.33(16)
N81-Sn2-N71	71.79(18)	N181-Sn4-N171	72.63(18)
N41-Sn2-O7	79.04(16)	N141-Sn4-O107	78.39(15)
N41-Sn2-O5	79.87(16)	N141-Sn4-O105	77.84(15)
N71-Sn2-N41	120.34(17)	N171-Sn4-N141	120.21(16)
N81-Sn2-O5	75.79(19)	N181-Sn4-O105	76.33(19)
O5-Sn2-O7	82.79(17)	O105-Sn4-O107	82.94(17)
N71-Sn2-05	142.21(16)	N171-Sn4-O105	143.59(16)
N41-Sn2-N81	147.9(2)	N141-Sn4-N181	145.7(2)

Structure **1b** was solved and refined in $P2_1$ as a racemic twin. The asymmetric unit contains two molecules $[Sn_2(bpza)_4]$. One of these exhibits a disordered pyrazole ring. Although a solution and refinement was also 'successful' in $P2_1/n$ (with a half as large c axis) additional reflections lying in between indicate in this case the larger c axis and $P2_1$ as correct space group.

Table S4. Selected bond distances and angles of [Sn(bdmpza)$_2$] (**2**), [Sn(bdmpza)F$_3$] (**3**) and [Sn(bdmpza)I$_3$].

Distance (Å)	**[Sn(bdmpza)$_2$] (2)**	**[Sn(bdmpza)F$_3$] (3)**	**[Sn(bdmpza)I$_3$][a]**
Sn-N11	2.8651(16)	2.201(2)	2.260(2)
Sn-N21	2.4569(16)	2.171(2)	2.270(2)
Sn-O1	2.1672(13)	2.0645(16)	2.087(2)
Sn-X1	-	1.9485(15)	2.7711(3)
Sn-X2	-	1.9566(14)	2.7754(3)
Sn-X3	-	1.9360(13)	2.7521(3)
N11-N12	1.362(2)	1.372(3)	1.376(3)
N21-N22	1.367(2)	1.372(3)	1.377(3)
C1-C2	1.556(3)	1.549(3)	1.553(4)
O2-C2	1.221(2)	1.211(3)	1.213(4)
O1-C2	1.270(2)	1.295(3)	1.302(3)
Angle (°)	**[Sn(bdmpza)$_2$] (2)[b]**	**[Sn(bdmpza)F$_3$] (3)**	**[Sn(bdmpza)I$_3$][a]**
Sn-N11-N12	116.72(11)	118.26(14)	118.17(14)
Sn-N21-N22	124.75(11)	117.52(14)	117.33(15)
Sn-O1-C2	134.96(12)	123.97(15)	126.01(19)
N11-Sn-O1	70.00(5)	83.14(7)	81.90(8)
N21-Sn-O1	75.22(5)	84.77(7)	81.22(8)
N21'-Sn-O1	77.71(5)		
N11-Sn-N21	69.00(5)	80.70(8)	81.04(8)
N11'-Sn-N21	122.20(5)		
N11'-Sn-N11	147.16(5)	-	-
N21'-Sn-N21	144.03(7)	-	-
O1'-Sn-O1	81.46(7)	-	-
X1-Sn-N21	-	94.12(7)	92.15(5)
X1-Sn-O1	-	92.53(7)	90.11(5)
X2-Sn-N11	-	90.40(7)	90.49(5)
X2-Sn-O1	-	91.30(6)	89.53(5)
x3-Sn-N11	-	88.84(7)	90.74(6)
X3-Sn-N21	-	89.97(7)	90.26(7)

[a]Data reported by Marchetti *et al.*[1]; [b]atoms deduced by symmetry are labelled with an apostrophe.

Table S5. Selected bond distances and angles of $[Fe(bdmpza)_2]$, $[Fe(bdmpza)_2]BF_4$, $[Ga(bdmpza)_2]ClO_4$ (**4**) and $[Ga(bpza)_2]GaCl_4$ (**5**)

Distance (Å)	**$[Fe(bdmpza)_2]$[a]**	**$[Fe(bdmpza)_2]BF_4$[b]**	**$[Ga(bdmpza)_2]ClO_4$ (4)**	**$[Ga(bpza)_2]GaCl_4$ (5)**
M-N11	2.169(3)	2.116(3)	2.0748(15)	2.064(2)
M-N21	2.212(3)	2.091(3)	2.0452(15)	2.047(2)
M-N31		2.144(3)	2.0649(16)	
M-N41		2.087(3)	2.0411(15)	
M-O1	2.080(3)	1.981(3)	1.9256(12)	1.9487(16)
M-O3		2.007(3)	1.9267(12)	
N11-N12	1.362(4)	1.366(4)	1.367(2)	1.359(3)
N21-N22	1.371(4)	1.357(4)	1.369(2)	1.359(3)
N31-N32		1.372(4)	1.365(2)	
N41-N42		1.374(4)	1.367(2)	
C1-C2	1.574(4)	1.540(5)	1.557(2)	1.548(4)
C3-C4		1.558(6)	1.554(2)	
O2-C2	1.234(4)	1.222(5)	1.209(2)	1.217(3)
O4-C4		1.235(5)	1.215(2)	
O1-C2	1.261(4)	1.279(5)	1.288(2)	1.296(3)
O3-C4		1.274(5)	1.290(2)	
Angle (◦)	**$[Fe(bdmpza)_2]$[a]**	**$[Fe(bdmpza)_2]BF_4$[b]**	**$[Ga(bdmpza)_2]ClO_4$ (4)**	**$[Ga(bpza)_2]GaCl_4$ (5)**
M-N11-N12	116.3(2)	116.2(2)	116.08(11)	116.64(15)
M-N21-N22	115.8(2)	116.2(2)	116.53(11)	116.55(15)
M-N31-N32		115.7(2)	115.71(11)	
M-N41-N42		116.7(2)	115.64(11)	
M-O1-C2	119.8(2)	122.6(2)	122.54(11)	122.15(16)
M-O3-C4		123.2(3)	121.62(11)	
N11-M-O1	84.36(10)	86.95(12)	87.70(6)	87.39(8)
N11-M-O3			90.37(6)	
N31-M-O3		85.20(12)	88.43(6)	
N21-M-O1	86.36(10)	86.31(11)	88.08(6)	87.75(8)
N41-M-O3		88.07(13)	88.71(6)	
N11-M-N21	84.05(10)	84.98(12)	86.58(6)	86.56(8)
N31-M-N41		84.32(13)	86.36(6)	

[a]Data reported by Beck *et al*.[2]

[b]Data according to Pflock *et al*.[3]

Calculation Details of the Sn Complexes in the Oxidation States II, III and IV

Restricted and unrestricted DFT-calculations were carried out by using the Jaguar 9.1.013 software[4] running on Linux 2.6.18-238.el5 SMP (x86_64) on five AMD Phenom II X6 1090T processor workstations (Beowulf-cluster) parallelised with OpenMPI. The molecular structure of [Sn(bdmpza)$_2$] (**2**) was used as starting geometry for the calculation of the tin(II) and tin(III) compounds. MM2-optimised structures were used for the calculation of the tin(IV) compounds. Complete geometry optimisations were carried out on the LACVP* (Hay-Wadt effective core potential (ECP) basis on heavy atoms, 6-31G* for all other atoms) basis set and with the PBE0 density functional. All calculated structures were proven to be true minima by the absence of imaginary frequencies. Plots were obtained using Maestro 10.5.013, the graphical interface of Jaguar. NMR shifts have been calculated with ADF 2016.103[5] on the TZ2P basis set (all-electron) and the KT2 density functional under consideration of relativistic effects with spin-orbit ZORA[6] on the geometry of the LACVP*/PBE0- optimised structures.

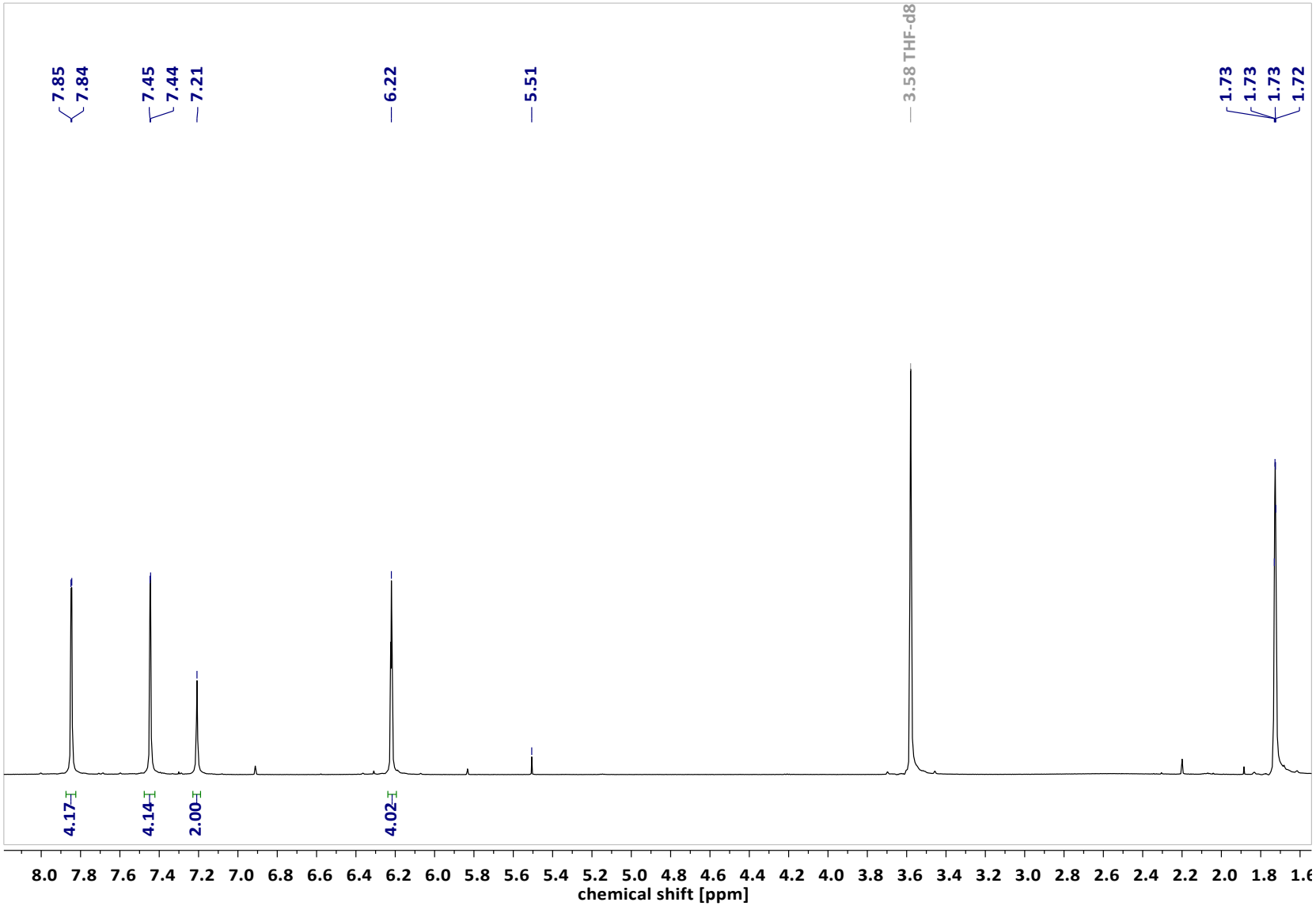

Figure S1. ^{1}H NMR spectrum of [Sn(bpza)$_2$] (**1**) in thf-d$_8$ used for DOSY measurements and molecular mass determination.

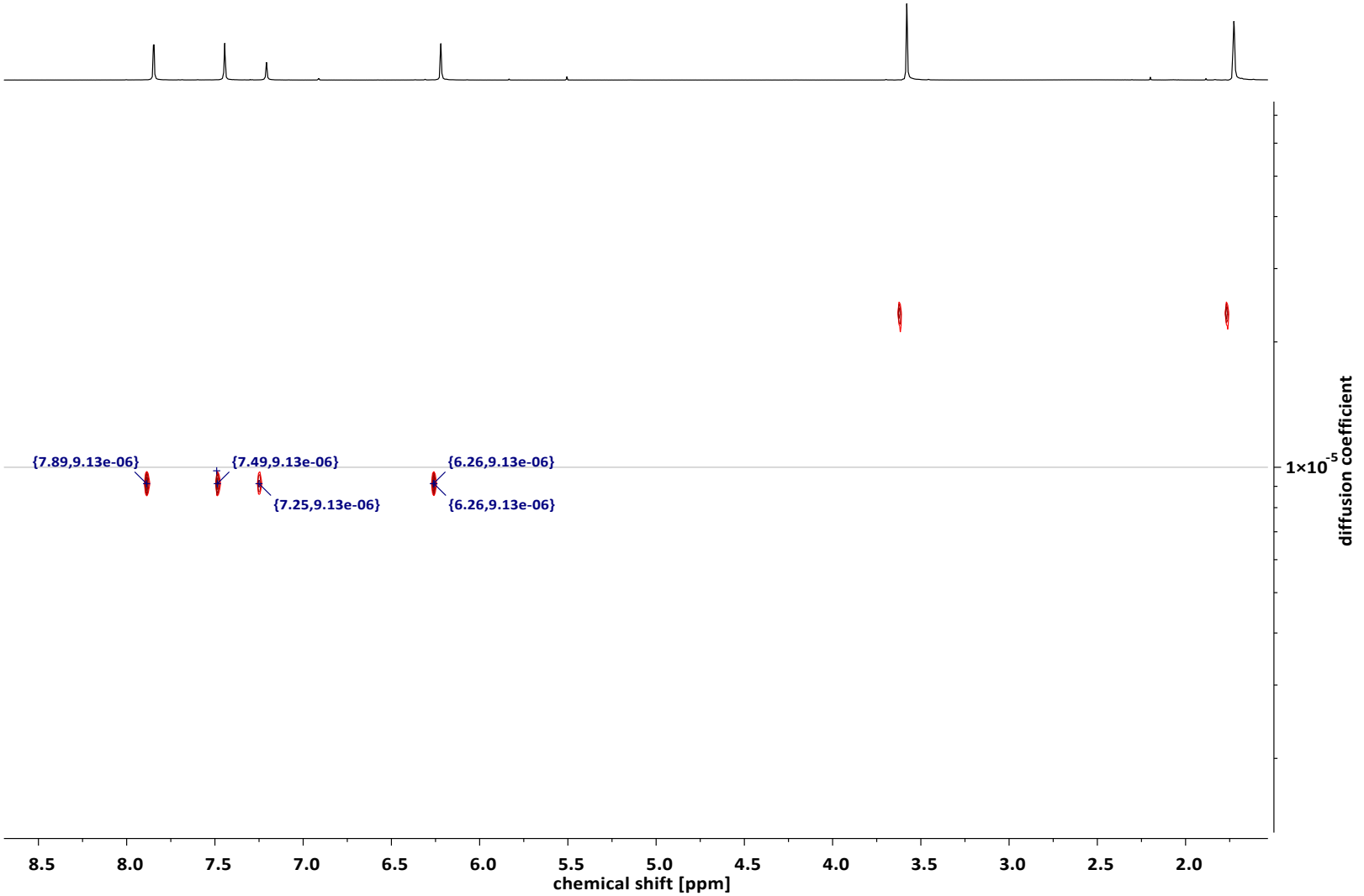

Figure S2. DOSY transform spectrum of [Sn(bpza)$_2$] (**1**) in thf-d$_8$ used molecular mass determination.[7]

Report Molecular Weight Determination *via* DOSY measurements

solvent: thf-d_8
analysis as: sole compound
formula: $C_{16}H_{14}N_8O_4Sn_1$

Results:

Integral region	$logD_x$	MD_w	χ	MW_{calc}	$MW_{det(merge)}$	MW_{corr}
7.953 to 7.807 ppm 7.558 to 7.421 ppm 7.301 to 7.181 ppm 6.323 to 6.194 ppm	-9,03079	6,75E+29	1,395375	501,05	353,38	**493,10**

Comments:
The determination of the molecular weight was carried out using the method described in reference [8a], where a molecular weight MW_{det} is calculated with $logD_x$ (D = diffusion coefficient) following the "ECC merge-concept" which is corrected for molecules with a high van-der Waals density MD_w (g/(mol*m^3) by a correction factor χ to obtain the result MW_{corr}. **The Sn complex obviously is a monomeric species in solution.**

Molecular weight determination:

ECC extended concept: ECC merge
internal reference: all residual signals of deuterated THF

Supplement

Diffusion measurements

Diffusion measurements were conducted on a Bruker AVANCE NMR spectrometer operating at 600.13 MHz for proton resonance equipped with a 5 mm PABDO BB/19F-1H/D probe with Z-GRD and actively shielded gradient coil with a maximum gradient strength of 5.3500094 G/mm (at 10 A).

Parameter optimization was carried out empirically employing the pulse programme ledbpgp2s1D using stimulated echo and LED (D21 = 5 ms, longitudinal eddy current delay as a Z-filter) with bipolar gradient pulses (P30) and two spoiling gradients (P19 = 600 µs) leading to values for gradient pulse length (P30 = adjusted [µs], in case of bipolar gradients *little DELTA*0.5*) and diffusion time (D20 = 60 ms, *big DELTA*). Delay for gradient recovery was set to 200 µs.

The diffusion experiment was executed with variable gradients from 2% to 98% gradient strength with 32 increment values (difframp calculated with the AU-program *DOSY*). In this case the pulse program ledbpgp2s was applied for data aquiring of this pseudo-2D Experiment. Data processing was performed with the T1/T2 software package (SimFit) of TopSpin (version 3.2, Bruker Biospin) by fitting area data (integration of all peaks of interest of the same molecule) of diffusion decays. From these Stejskal-Tanner fitting curves calculated diffusion constants were obtained and assimilated statistically.

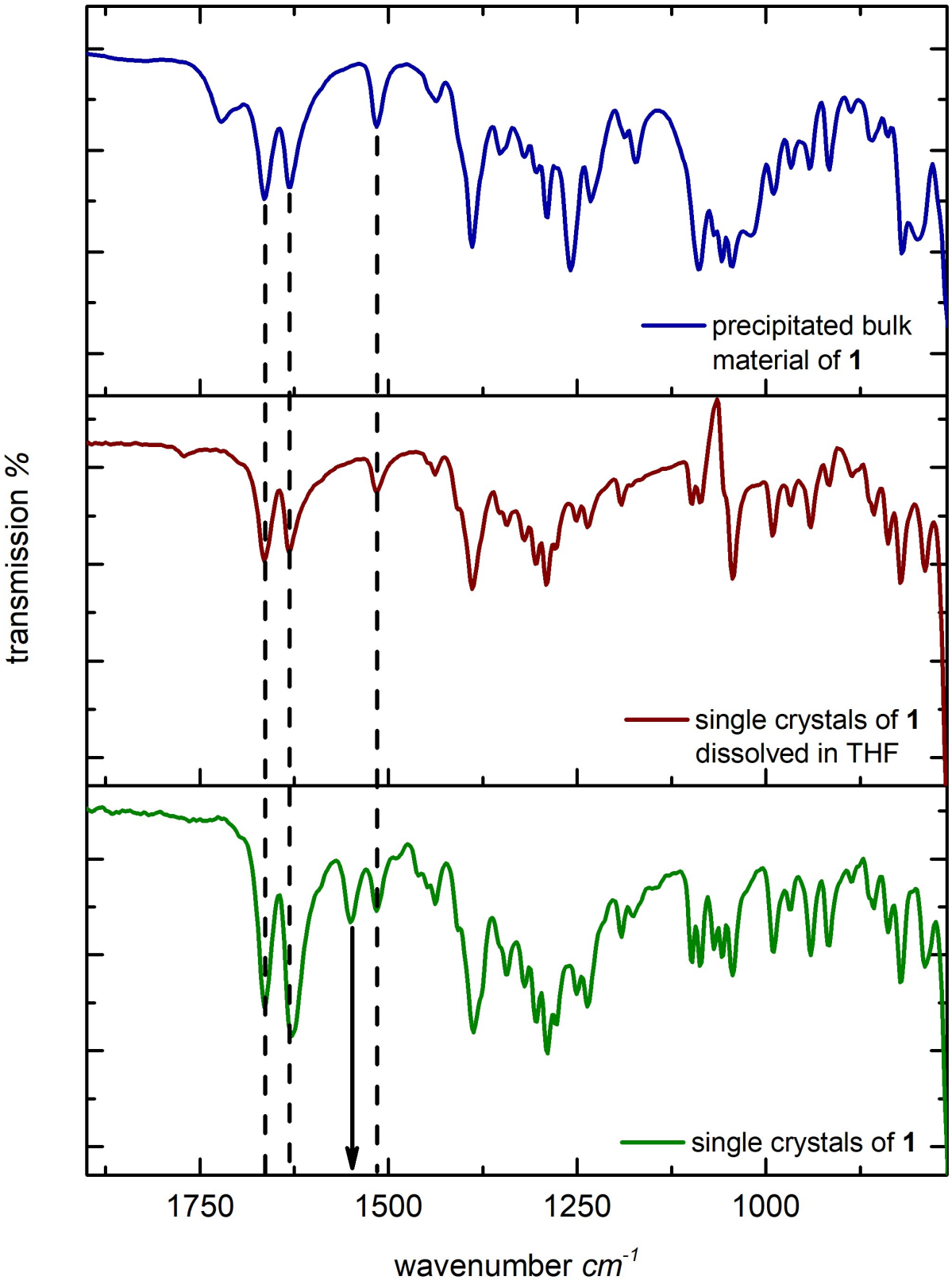

Figure S3. IR data of $[Sn(bpza)_2]$ (**1**) and $[Sn_2(bpza)_4]$ (**1b**).

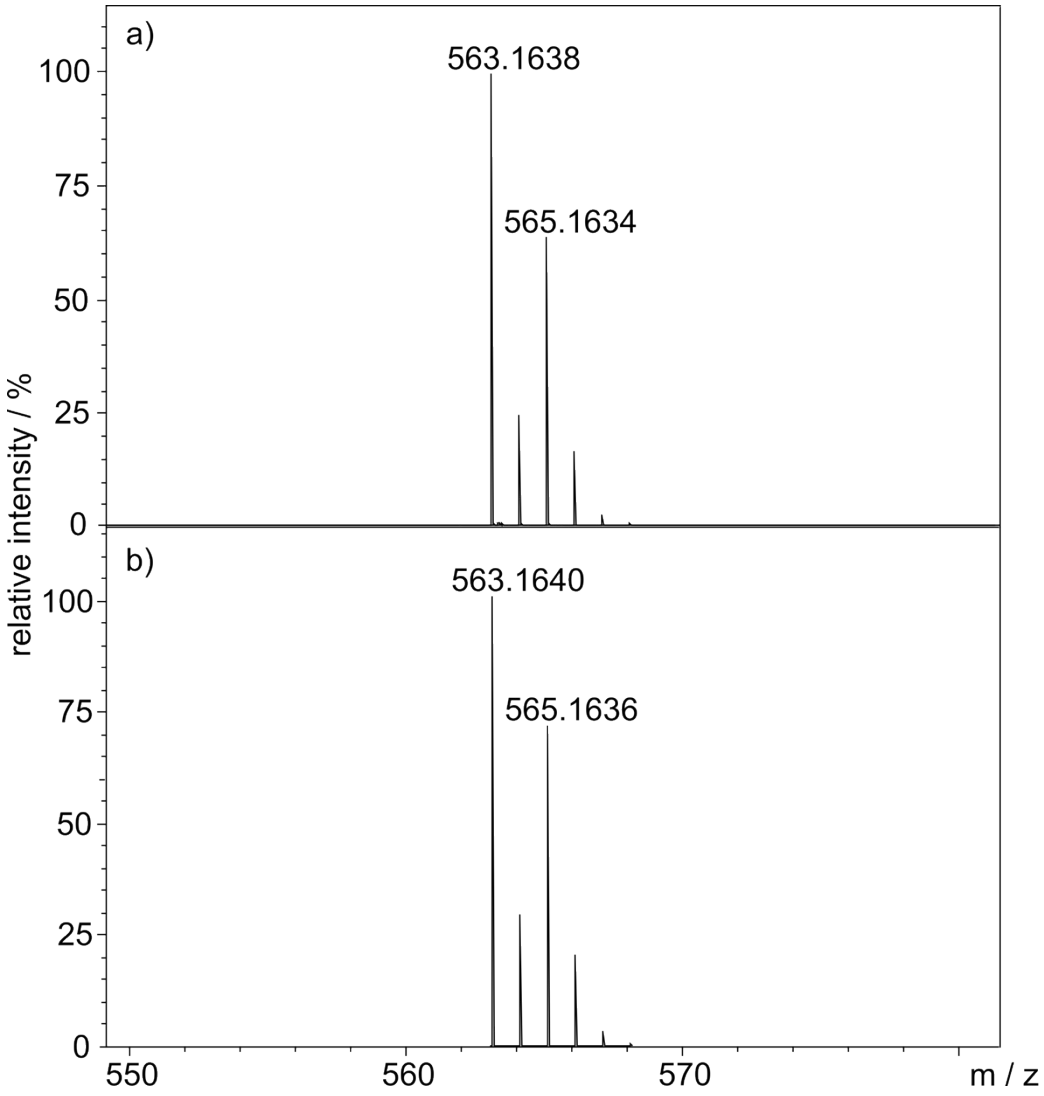

Figure S4. a) Observed and b) calculated MS spectra of the detectable complex cation of $[Ga(bdmpza)_2]ClO_4$ (**4**); ESI MS spectrum measured in acetonitrile.

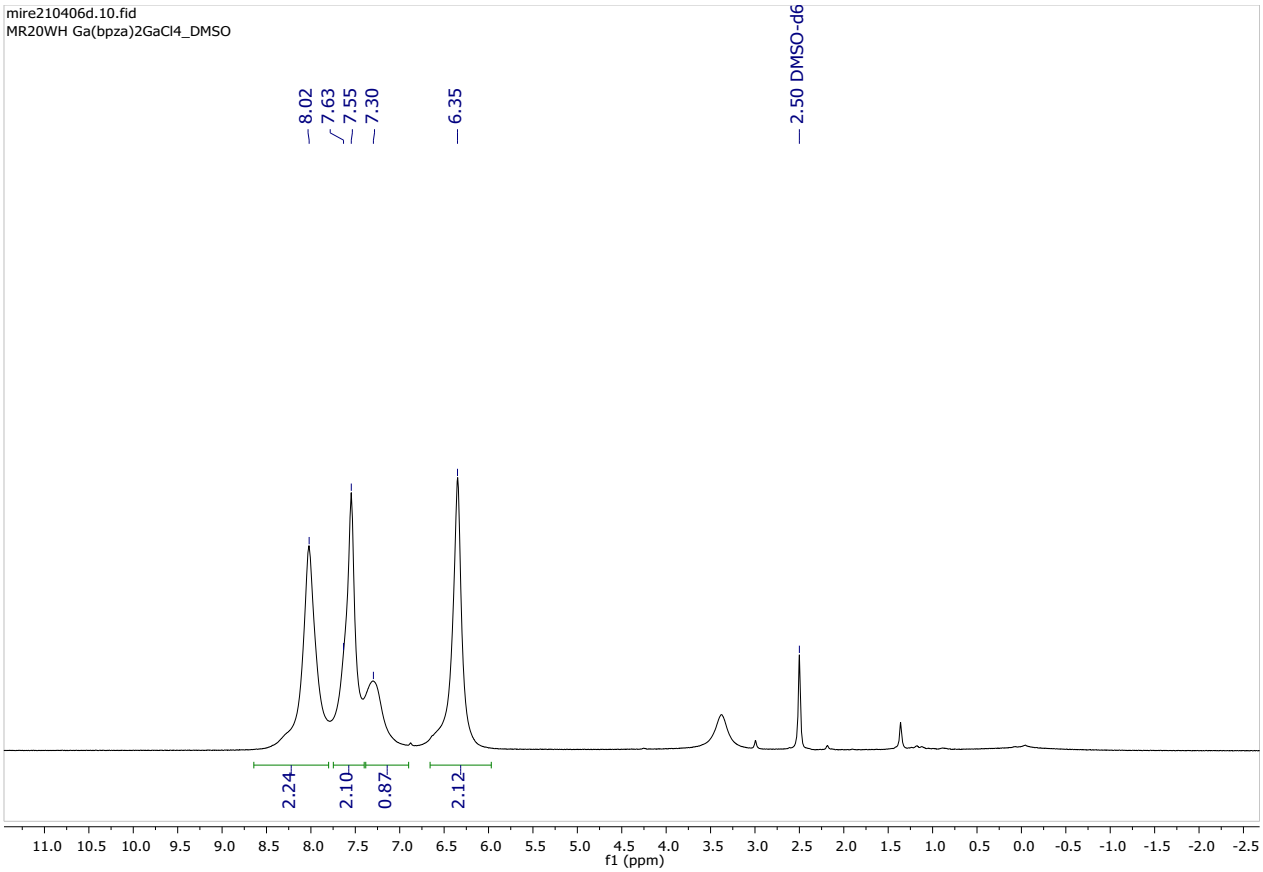

Figure S5. ^{1}H NMR of [Ga(bpza)$_2$]GaCl$_4$ (**5**) in dmso-*d*^{6} at RT.

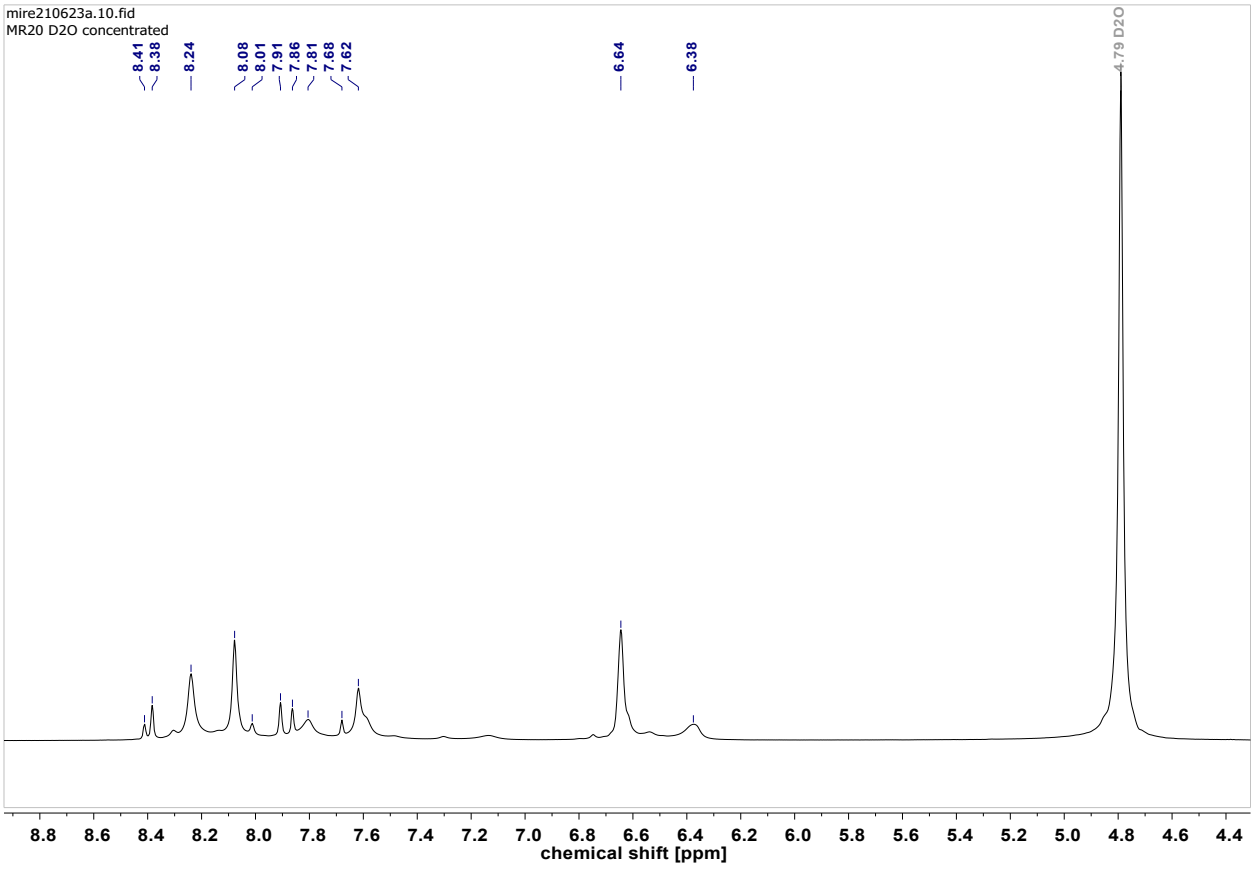

Figure S6. ^{1}H NMR of [Ga(bpza)$_2$]GaCl$_4$ (**5**) in D$_2$O at RT.

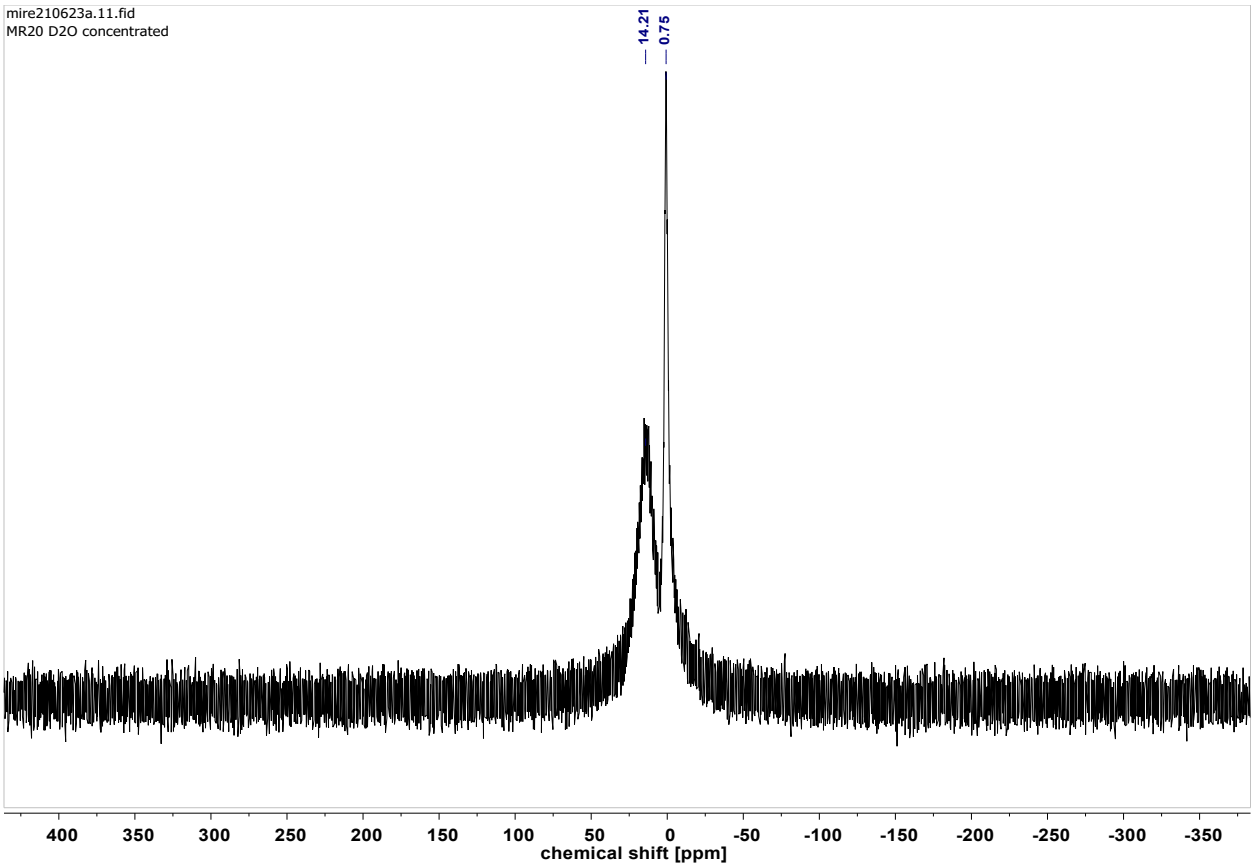

Figure S7. ^{71}Ga NMR of $[Ga(bpza)_2]GaCl_4$ (**5**) in D_2O at RT.

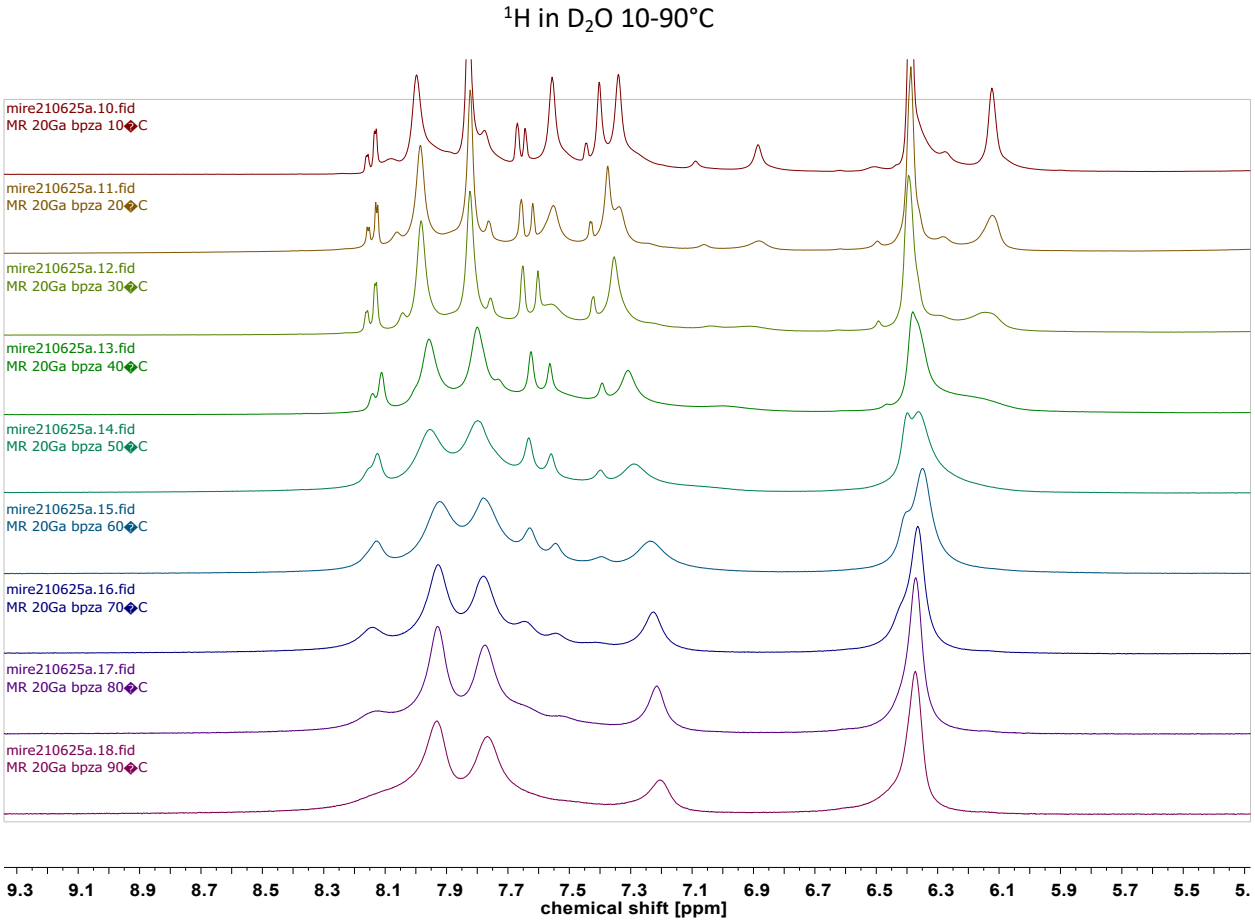

Figure S8. ^{1}H NMR of $[Ga(bpza)_2]GaCl_4$ (**5**) in D_2O (10°C to 90°C).

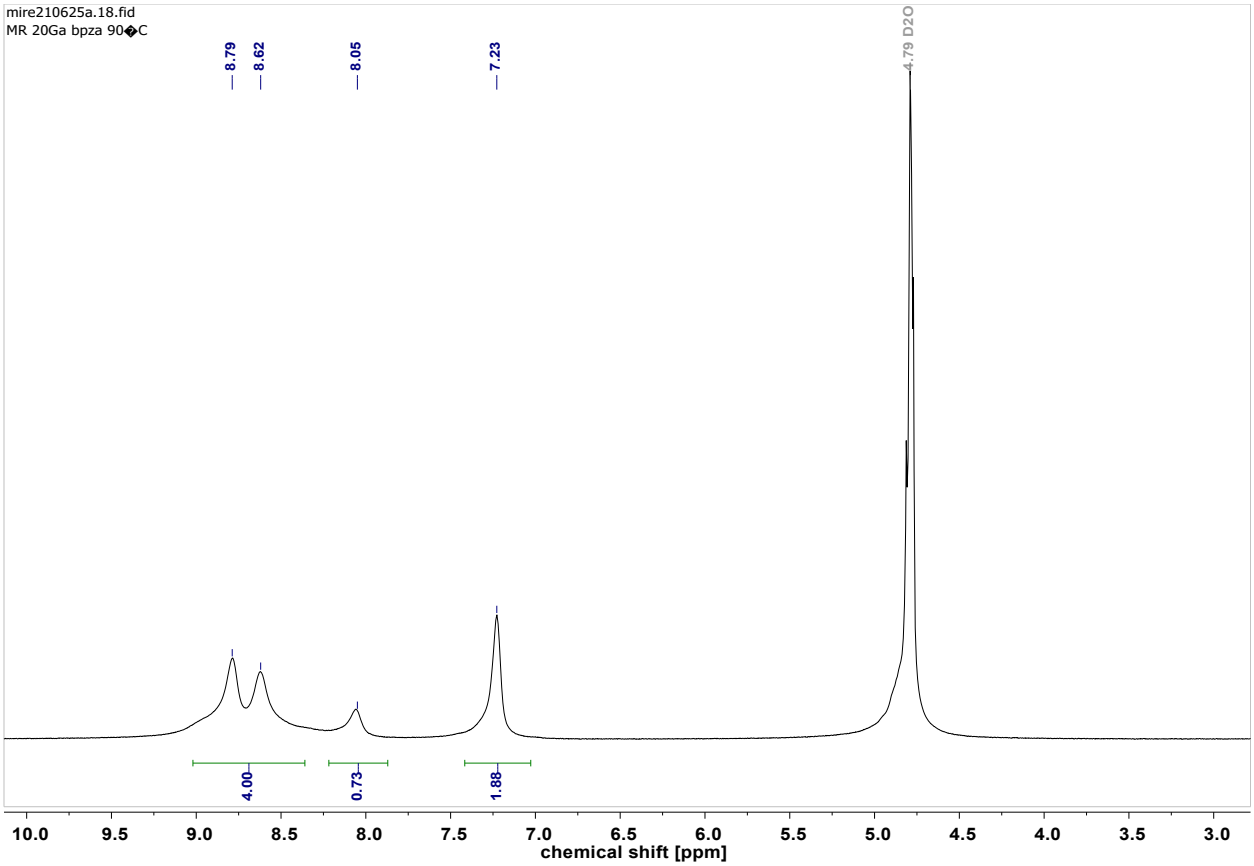

Figure S9. ^{1}H NMR of $[Ga(bpza)_2]GaCl_4$ (**5**) in D_2O at 90°C.

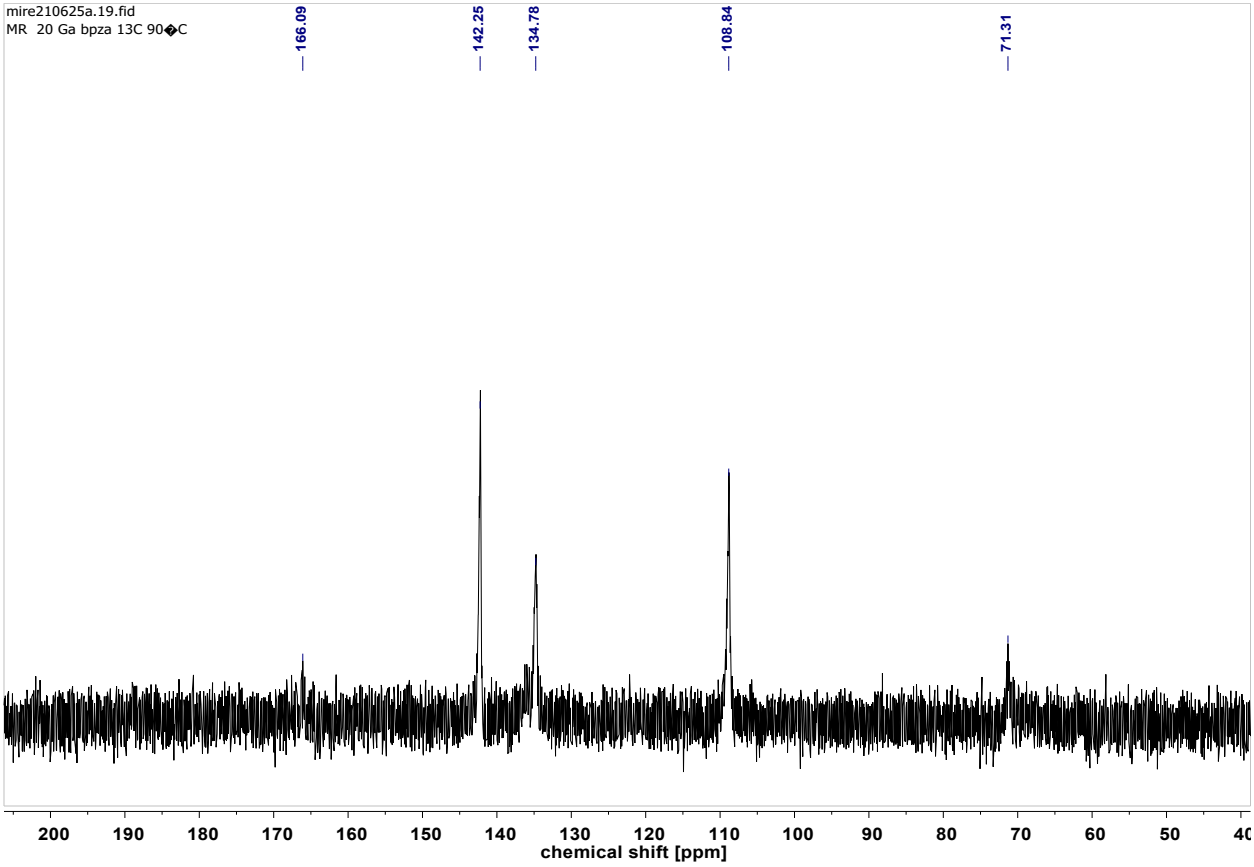

Figure S10. ^{13}C NMR of $[Ga(bpza)_2]GaCl_4$ (**5**) in D_2O at 90°C.

References

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[2] A. Beck, B. Weibert, N. Burzlaff, *Eur. J. Inorg. Chem.,* 2001, 521.

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