Appendices – DOSY studies

**General procedures for DOSY experiments**

DOSY experiments were performed on a Bruker AVANCE 400 NMR spectrometer operating at 400.13 MHz for proton resonance under TopSpin (version 2.0, Bruker Biospin, Karlsruhe) and equipped with a BBFO-z-atm probe with actively shielded zgradient coil capable of delivering a maximum gradient strength of 54 G/cm. Typically diffusion ordered NMR data were acquired using the Bruker pulse program dstegp3s employing a double stimulated echo with three spoiling gradients. Sine-shaped gradient pulses were used with a typical duration, P30, of 3 ms (25 ºC) or 5.5 ms (40 °C) together with a typical diffusion period of 100 ms (D20). Gradient recovery delays of 200 μs followed the application of each gradient pulse. Data were systematically accumulated by linearly varying the diffusion encoding gradients over a range from 2% to 95% for 64 gradient increment values. The signal decay dimension on the pseudo-2D data was generated by Fourier transformation of the time-domain data. DOSY plots were generated by use of the DOSY processing module of TopSpin. Parameters were optimized empirically to find the best quality of data for presentation purposes. Diffusion coefficients were calculated by fitting intensity data to the Stejskal-Tanner expression with estimates of errors taken from the variability in the calculated diffusion coefficients by consideration of different NMR responses for the same molecules of interest.

**DOSY NMR studies**

To gain some information about the nature in solution of the compound [{(THF)6Mg2Cl2}+{Zn2Et5}‒] (4**1**) and whether its solid X-ray structure is retained or not, its diffusion properties were studied using Diffusion-Ordered NMR Spectroscopy (DOSY). DOSY techniques can be used to identify individual components of solution mixtures (comparable to chromatography in NMR terms), and to estimate their sizes, that are inversely proportional to their diffusion coefficients (D).[[1]](#footnote-1) To obtain accurate hydrodynamic dimensions and avoid the misleading results that single diffusion measurements can produce,2b DOSY measurements can be run in the presence of internal standards of known molecular weight.[[2]](#footnote-2)

The relationship between the diffusion coefficient of a molecule (*D*) and its molecular weight (FW) (assuming the approximation that the size of a molecule is proportional to its FW) can be easily linearised by the expression **log D *=* *A* log FW + *B***. Using internal standards of known FW and measuring their diffusion coefficients a calibration curve can be generated. If the correlation between log *D* and log FW of the linear squares fit to the internal standards can be established, and the empirical FW of the unknown species can be calculated from the curve. The question emerging from this treatment of the data is how accurate is the approximation that the size of a molecule is proportional to its FW, especially for zinc-containing species where a single atom is much heavier than the rest of the atoms present (C, O and H).

To elucidate, if this FW-size proportionality is maintained for zinc containing complexes, the diffusion properties of a Zn-species of known structure, [(TMEDA)ZnEt2], were studied at 25 ºC in d8-THF in the presence of internal standards. Therefore, the 1H DOSY NMR spectrum of [(TMEDA)ZnEt2] with internal references present (TPhN; 1,2,3,4-tetraphenylnaphthlene, PhN; 1-phenylnaphthalene, and TMS; tetramethylsilane) was recorded in d8-THF at 25 °C (**Figure S1**). All the different components of the mixture separate clearly in the diffusion dimension with a relative size sequence of TPhN >> PhN ~ [(TMEDA)ZnEt2] >> TMS, according to their increasing *D* values [D(TPhN) = 8.92(7) x 10−10 m2 s−1 << D(PhN) = 1.51(3) x 10−9 m2 s−1 ~ D[(TMEDA)ZnEt2] = 1.52(1) x 10−9 m2 s−1 << D(TMS) = 2.35 x 10−9 m2 s−1]. A correlation between log *D* and log FW of the linear squares fit to the internal standards can be established (**Figure S2**: log *D* = –0.6076∙log FW – 7.4372; r = 0.9928). From this calibration curve the size inferred for [(TMEDA)ZnEt2] (in terms of its FW) is 187 g mol-1, which represents a 22 % error with respect to the real molecular weight of [(TMEDA)ZnEt2] (239.72 g mol-1). Note that the DOSY plot shows how all the resonances of [(TMEDA)ZnEt2] exhibit cross points lying in the same line of the second dimension (Daverage = 1.52(1) x 10−09 m2 s−1), which implies that the TMEDA and Et groups belong to the same molecule, [(TMEDA)ZnEt2], the structure of which is retained in solution. This data indicates that for this Zn containing molecule the size-FW proportionality is compromised.



TPhN

(432.55 g mol-1)

PhN

(204.27 g mol-1)

TMS

(88.22 g mol-1)

[(TMEDA)Zn(CH2CH3)2]

**Figure S1.** 1H DOSY NMR spectrum of [(TMEDA)ZnEt2], TPhN, PhN and TMS at 25 °C in d8-THF.

TPhN

(432.55 g mol-1)

PhN

(204.27 g mol-1)

TMS

(88.22 g mol-1)

**Figure S2.** log *D* – log FW representation from the 1H DOSY data obtained for the mixture of [(TMEDA)ZnEt2], TPhN, PhN and TMS at 25 °C in d8-THF (data for the components of [(TMEDA)ZnEt2] is not included).

Adopting a different approach, the molecular sizes of the species present were expressed by molar volumes instead of FW, and therefore diffusion coefficients (*D*) were correlated with molar volumes (*V*), using the expression **log D *=* *A* log V + *B***. The calculated volumes for the internal standard used are 358.50 cm3 mol-1 (TPhN), 163.50 cm3 mol-1 (PhN) and 101.50 cm3 mol-1 (TMS).[[3]](#footnote-3) The correlation between log *D* and log *V* of the linear squares fit to the internal standards can also be perfectly established (**Figure S3**: log *D* = –0.7583∙log V – 7.1208; r = 0.9923). From this calibration curve the size of [(TMEDA)ZnEt2] (in terms of its volume) is 173 cm3 mol-1, which represents a 9 % error with respect to the calculated volume for [(TMEDA)ZnEt2] (189.30 cm3 mol-1). A similar study was carried out in the non polar solvent D12-toluene and the size values inferred for [(TMEDA)ZnEt2] were 199 g mol-1 (using the FW approach; 17 % error respect to the real value) and 182 cm3 mol-1 (using the *V* approach; 4 % error respect to the calculated value). From this comparative study it is obvious that a log *D* – log *V* correlation is more accurate than log *D* – log FW, and therefore the data extracted from the diffusion properties of our complex of interest **41** would be treated in this way.

TPhN

(358.50 cm3 mol-1)

PhN

(163.50 cm3 mol-1)

TMS

(101.50 cm3 mol-1)

**Figure S3.** log *D* – log *V* representation from the 1H DOSY data obtained for the mixture of [(TMEDA)ZnEt2], TPhN, PhN and TMS at 25 °C in [D8]-THF (data for the components of [(TMEDA)ZnEt2] is not included).

**Diffusion study of [{(THF)6Mg2Cl2}+{Zn2Et5}‒] (41)**

1H DOSY NMR spectrum of **41** with internal references present (TPhN, PhN and TMS) was recorded in d8-THF at 25 °C and at 40 °C. The DOSY plot at 25 °C (**Figure S4**) shows that all the different components separate in the diffusion dimension with a relative size sequence of TPhN >> PhN ~ **41** >> TMS, according to their increasing *D* values [D(TPhN) = 7.03(8) x 10−10 m2 s−1 << D(PhN) = 1.18(2) x 10−9 m2 s−1 ~ D(**41**) = 1.24(3) x 10−9 m2 s−1 << D(TMS) = 1.77 x 10−9 m2 s−1]. The correlation between log *D* and log *V* of the linear squares fit to the internal standards can be established (**Figure S5**: log *D* = –0.7236∙log V – 7.3112; r = 0.9948). From this calibration curve the average size of the “Zn-(CH2CH3)” species present in solution (in terms of its *V*) is 160 cm3 mol-1. The same procedure was followed at 40 °C. (**Figure S6**) shows the DOSY plot at this lower temperature, where all the different components separate in the diffusion dimension with a relative size sequence of TPhN > **41** > PhN >> TMS, according to their increasing D values [D(TPhN) = 1.79(1) x 10−10 m2 s−1 < D(**41**) = 2.69(1) x 10−10 m2 s−1 < D(PhN) = 3.3(1) x 10−10 m2 s−1 << D(TMS) = 6.15 x 10−10 m2 s−1]. It is clear that while at 25 ºC the size of the “Zn-(CH2CH3)” species is close to PhN, at 40 ºC the Zn containing species increase its size considerably, being allocated in between TPhN and PhN. The volume of “Zn-(CH2CH3)” estimated from the calibration curve generated at 40 ºC (**Figure S7**: log *D* = –0.9603∙log V – 7.3096; r = 0.9824), gives in fact a value of 226 cm3 mol-1. It is therefore evident that going to lower temperature some sort of aggregation process, involving the “Zn-(CH2CH3)” species, occurs.



TPhN

(358.50 cm3 mol-1)

PhN

(163.50 cm3 mol-1)

TMS

(101.50 cm3 mol-1)

“Zn-(CH2CH3)”

THF

**Figure S4.** 1H DOSY NMR spectrum of **41**, TPhN, PhN and TMS at 25 °C in d8-THF.

TPhN

(358.50 cm3 mol-1)

PhN

(163.50 cm3 mol-1)

TMS

(101.50 cm3 mol-1)

**Figure S5.** log *D* – log *V* representation from the 1H DOSY data obtained for the mixture of **41**, TPhN, PhN and TMS At 25 °C in d8-THF (data for the components of **41** is not included).



THF

“Zn-(CH2CH3)”

TMS

(101.50 cm3 mol-1)

PhN

(163.50 cm3 mol-1)

TPhN

(358.50 cm3 mol-1)

**Figure S6.** 1H DOSY NMR spectrum of **41**, TPhN, PhN and TMS at 40 °C in d8-THF.

TPhN

(358.50 cm3 mol-1)

PhN

(163.50 cm3 mol-1)

TMS

(101.50 cm3 mol-1)

**Figure S7.** log *D* – log *V* representation from the 1H DOSY data obtained for the mixture of **41**, TPhN, PhN and TMS At 40 °C in d8-THF (data for the components of **41** is not included).

**Diffusion study of ZnEt2**

1H DOSY NMR spectrum of ZnEt2 with internal references present (TPhN, PhN and TMS) was recorded in d8-THF at 25 °C and at 40 °C. **Figure S8** shows the DOSY plot at 25 °C where all the different components separate in the diffusion dimension with a relative size sequence of TPhN >> PhN > ZnEt2 > TMS, according to their increasing D values [D(TPhN) = 9.2(3) x 10−10 m2 s−1 << D(PhN) = 1.51(3) x 10−9 m2 s−1 < D(ZnEt2) = 1.86(3) x 10−9 m2 s−1 < D(TMS) = 2.28 x 10−9 m2 s−1]. The correlation between log *D* and log V of the linear squares fit to the internal standards can be established (**Figure S9**: log *D* = –0.7144∙log V – 7.2202; r = 0.9926). From this calibration curve the average size of the “Zn-(CH2CH3)” species present in solution (in terms of its V) is 131 cm3 mol-1. The same procedure was followed at 40 °C. **Figure S10** shows the DOSY plot at the lower temperature, where all the different components separate in the diffusion dimension with a relative size sequence of TPhN >> PhN > ZnEt2 > TMS, according to their increasing D values [D(TPhN) = 2.51(7) x 10−10 m2 s−1 << D(PhN) = 4.52(2) x 10−10 m2 s−1 < D(ZnEt2) = 5.46(2) x 10−10 m2 s−1 < D(TMS) = 7.49 x 10−10 m2 s−1]. The volume of “Zn-(CH2CH3)” estimated from the calibration curve generated at 40 ºC (**Figure S11**: log *D* = –0.8528∙log V – 7.4311; r = 0.9906), gives a value of 141 cm3 mol-1, similar to the one obtained at 25 ºC. Therefore, the aggregation process observed for the complex **41** going to lower temperature does not occur for ZnEt2.



TPhN

(358.50 cm3 mol-1)

PhN

(163.50 cm3 mol-1)

TMS

(101.50 cm3 mol-1)

“Zn-(CH2CH3)”

THF

**Figure S8.** 1H DOSY NMR spectrum of ZnEt2, TPhN, PhN and TMS at 25 °C in d8-THF.

TPhN

(358.50 cm3 mol-1)

PhN

(163.50 cm3 mol-1)

TMS

(101.50 cm3 mol-1)

**Figure S9.** log D – log V representation from the 1H DOSY data obtained for the mixture of ZnEt2, TPhN, PhN and TMS At 25 °C in d8-THF (data for the components of ZnEt2 is not included).



TPhN

(358.50 cm3 mol-1)

PhN

(163.50 cm3 mol-1)

TMS

(101.50 cm3 mol-1)

THF

“Zn-(CH2CH3)”

**Figure S10.** 1H DOSY NMR spectrum of ZnEt2, TPhN, PhN and TMS at 40 °C in d8-THF.

**Figure S11.** log D – log V representation from the 1H DOSY data obtained for the mixture of ZnEt2, TPhN, PhN and TMS At 40 °C in d8-THF (data for the components of ZnEt2 is not included) .

TPhN

(358.50 cm3 mol-1)

PhN

(163.50 cm3 mol-1)

TMS

(101.50 cm3 mol-1)

**Diffusion study of ZnEt2 + MgCl2**

1H DOSY NMR spectrum of ZnEt2 + MgCl2 with internal references present (TPhN, PhN and TMS) was recorded in d8-THF at 25 °C and at 40 °C. **Figure S12** shows the DOSY plot at 25 °C where all the different components separate in the diffusion dimension with a relative size sequence of TPhN >> ZnEt2 + MgCl2 ~ PhN >> TMS, according to their increasing D values [D(TPhN) = 7.45(6) x 10−10 m2 s−1 << D(ZnEt2 + MgCl2) = 1.28(4) x 10−9 m2 s−1 ~ D(PhN) = 1.28(2) x 10−9 m2 s−1 << D(TMS) = 2.04 x 10−9 m2 s−1]. The correlation between log *D* and log V of the linear squares fit to the internal standards can be established (**Figure S13**: log *D* = –0.787∙log V – 7.1269; r = 0.9903). From this calibration curve the average size of the “Zn-(CH2CH3)” species present in solution (in terms of its V) is 175 cm3 mol-1. The same procedure was followed at 40 °C. **Figure S14** shows the DOSY plot at that lower temperature, where all the different components separate in the diffusion dimension with a relative size sequence of TPhN >> ZnEt2 + MgCl2 ~ PhN >> TMS, according to their increasing D values [D(TPhN) = 2.0(1) x 10−10 m2 s−1 << D(ZnEt2 + MgCl2) = 3.62(2) x 10−10 m2 s−1 ~ D(PhN) = 3.55(5) x 10−10 m2 s−1 << D(TMS) = 6.10 x 10−10 m2 s−1]. The volume of “Zn-(CH2CH3)” estimated from the calibration curve generated at 40 ºC (**Figure S15:** log *D* = –0.8667∙log V – 7.4971; r = 0.9844), gives the same value obtained at 25 ºC, 175 cm3 mol-1. Again, the aggregation process observed for the complex **41** going to lower temperature does not occur for ZnEt2 + MgCl2. This data provides a clear evidence of the interaction between MgCl2 and ZnEt2, as 175 cm3 mol-1 is significantly higher to the volume inferred for solutions of just ZnEt2 (V= 131-141 cm3mol-1).



TPhN

(358.50 cm3 mol-1)

TMS

(101.50 cm3 mol-1)

THF

“Zn-(CH2CH3)”

PhN

(163.50 cm3 mol-1)

**Figure S12.** 1H DOSY NMR spectrum of ZnEt2 + MgCl2, TPhN, PhN and TMS at 25 °C in d8-THF.

TPhN

(358.50 cm3 mol-1)

PhN

(163.50 cm3 mol-1)

TMS

(101.50 cm3 mol-1)

**Figure S13.** log D – log V representation from the 1H DOSY data obtained for the mixture of ZnEt2 + MgCl2, TPhN, PhN and TMS At 25 °C in d8-THF (data for the components of ZnEt2 + MgCl2 is not included).



“Zn-(CH2CH3)”

THF

TMS

(101.50 cm3 mol-1)

PhN

(163.50 cm3 mol-1)

TPhN

(358.50 cm3 mol-1)

**Figure S14.** 1H DOSY NMR spectrum of ZnEt2 + MgCl2, TPhN, PhN and TMS at 40 °C in d8-THF.

TPhN

(358.50 cm3 mol-1)

PhN

(163.50 cm3 mol-1)

TMS

(101.50 cm3 mol-1)

**Figure S15.** log D – log V representation from the 1H DOSY data obtained for the mixture of ZnEt2 + MgCl2, TPhN, PhN and TMS At 40 °C in d8-THF (data for the components of ZnEt2 + MgCl2 is not included).

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Entry** | **Possible species** | **V(cm3/mol) calculated using DFT** | **V predicted by DOSY studies of solutions of 1 in [D8]-THF** | | **V predicted by DOSY studies of solutions of ZnEt2 in [D8]-THF** | | **V predicted by DOSY studies of solutions of ZnEt2+MgCl2 in [D8]-THF** | |
|  |  |  | **160.33** (25 oC) | **226.31** (-40 oC) | **130.48** (25 oC) | **140.69** (-40 oC) | **175.06**  (25 oC) | **174.99**  (-40 oC) |
|  |  |  | error % | error % | error % | error % | error % | error % |
| 1 | {Zn2Et5}- | 232.00 | 44.70 | 2.51 | 77.80 | 64.90 | 32.53 | 32.57 |
| 2 | {ZnEt3}- | 119.30 | -25.59 | -47.28 |  |  | -31.85 | -31.82 |
| 3 | ZnEt2 | 77.80 | -51.48 | -65.62 | -40.37 | -44.70 | -55.56 | -55.54 |
| 4 | ZnEt2(THF) | 161.80 | 0.92 | -28.51 | 24.00 | 15.00 | -7.57 | -7.54 |
| 5 | ZnEt2(THF)2 | 196.50 | 22.56 | -13.17 | 50.60 | 39.67 | 12.25 | 12.29 |
| 6 | {ZnEt2Cl}- | 114.40 | -28.65 | -49.45 |  |  | -34.65 | -34.62 |
| 7 | [ZnEt2MgCl2] | 142.90 | -10.87 | -36.86 |  |  | -18.37 | -18.34 |
| 8 | [ZnEt2MgCl2(THF)2] | 270.20 | 68.53 | 19.39 |  |  | 54.35 | 54.40 |

**Table S1.** Some plausible species of “Zn2Et5” in d8-THF solution with their respective calculated volumes per mol (V), and the relative error for every consideration with respect to the volumes predicted through DOSY studies of **41**, ZnEt2 and ZnEt2 + MgCl2 in d8-THF solutions.

Several conclusions, some previously mentioned, can be extracted from this table:

1. For {Zn2Et5}- in solution, an evident aggregation process involving the “Zn-(CH2CH3)” species occurs going to lower temperature. This phenomenon does not occur or it is significantly less important for ZnEt2 or ZnEt2 + MgCl2.
2. At 25 ºC {Zn2Et5}- does not exist, at least in a large extent, as no species near its size appears in solution (error 31 %; entry 1). Therefore smaller aggregates should form, giving an equilibrium between the {Zn2Et5}- components (ZnEt2 and {ZnEt3}-) with different grades of THF solvation and/or chlorine addition the most probable scenario.
3. At -40 ºC {Zn2Et5}- seems to be the most plausible “Zn-(CH2CH3)“ species in solution (3 % error; entry 1). The presence of other higher aggregates (for example the mixed metal species [ZnEt2MgCl2(THF)2]; 16 % error; entry 8) in equilibrium with its smaller counterparts cannot be discarded.
4. ZnEt2 does not exist, at least as unique species in d8-THF, as much bigger species appear in solution (error -74(9) %; entry 3). THF solvated species (entries 4 and 5) give smaller errors (13-34 %) indicating that [(THF)xZnEt2] species, where x = 0, 1, 2, coexist in an equilibrium in which ZnEt2 is never fully solvated (entry 5, error 31(4) %).
5. ZnEt2 suffers a clear size increase in the presence of MgCl2 as its average volume of 136(7) cm3 mol-1 increases to 175(0) cm3 mol-1. This indicates that equilibriums involving species such as [ZnEt2Cl] or [MgCl2:ZnEt2], with different grades of THF solvation, have to be considered when studying the solution chemistry of “Zn2Et5” as MgCl2 is present.

**DFT calculations of molecular volumes**

DFT calculations were carried out using the Gaussian G03 computational package.[[4]](#footnote-4) Exploratory *ab initio* calculations at the Hartree Fock (HF) level were performed using the 6-31G\* basis set. The resultant optimised geometries were subjected to a frequency analysis and then refined further by density functional theory (DFT) calculations utilising the B3LYP functionals[[5]](#footnote-5) and the 6-311G(d,p)basis set.[[6]](#footnote-6) The total energy taken from the DFT calculation was adjusted by inclusion of the zero point energy value from the HF calculation modified by the factor 0.91.



**(TMEDA)ZnEt2**

Volume = 189.3 cm3 mol-1

N-Zn 2.468 Å; Zn-C 1.991 Å; C-C 1.539 Å; N-Zn-N 76.5 °; C-Zn-C 149.6 °; Zn-C-C 114.8 °.

**ZnEt2 {ZnEt3}-**

V=77.8 cm3 mol-1 V=119.3 cm3 mol-1

Zn-C 1.954 Å; C-C 1.539 Å Zn-C 2.058 Å; C-C 1.537 Å

**{Zn2Et5}-**

Geometry 1: the ZnEt2 portion has the Et groups twisted towards the ZnEt3- moiety



Geometry 2: the ZnEt2 portion has the Et groups twisted away from the ZnEt3- moiety

Energies Total/a.u. Relative/kcal mol-1

**Geometry 1**  -3954.549577 0.91

**Geometry 2** -3954.551027 0.00

Energy of Reaction: ZnEt2 + ZnEt3- = Zn2Et5-

For **Geometry 1** ΔE = -5.76 kcal mol-1

For **Geometry 2** ΔE = -6.67 kcal mol-1

**Volumes** {Zn2Et5}- **Geometry 1** 226.3 cm3 mol-1

**Geometry 2** 238.0 cm3 mol-1

**Average V= 232.15**

**ZnEt2(THF)** **ZnEt2(THF)2**

****

Volume =161.8 cm3 mol-1 Volume =196.5 cm3 mol-1

Zn-O 2.413 Å; Zn-C 1.965 Å; Zn-O 2.463 Å; Zn-C 1.978 Å;

C-Zn-C 165.9 °; O-Zn-C 97.1 ° C-Zn-C 159.3 °; O-Zn-C 96.9 °; O-Zn-O 78.7

**{ZnEt2Cl}- [ZnEt2MgCl2}**



Volume = 114.4 cm3 mol-1 Volume =142.9 cm3 mol-1

Zn-Cl 2.503 Å; Zn-C 1.995 Å; C-C 1.537 Å; Mg-Cl 2.218 Å; Mg-Clbr 2.247 Å;

Mg-Cbr 2.340 Å; Zn-Clbr 2.930 Å;

Zn-Cbr 2.021 Å; Zn-C 1.948 Å;

Cl-Zn-C 106.4 °; C-Zn-C 147.1 ° C-Zn-C 162.8 °; Cl-Mg-Cl 144.6 °

**[ZnEt2MgCl2(THF)2}**



Volume = 270.2 cm3 mol-1

Zn-C 1.957, 1.964 Å ; Zn..Cl 3.470, 3.578 Å; Mg-Cl 2.286, 2.284 Å;

Mg-O, 2.063, 2.063 Å; C-Zn-C, 172.7 °; O-Mg-O 106.2 °; Cl-Mg-Cl 128.6 °

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