Probing Ionic Association on Metal Oxide Clusters by Pulsed Field Gradient NMR Spectroscopy: The Example of Sn_{12}–Oxo Clusters

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Abstract: Pulsed field gradient ^1H NMR spectroscopy has been applied to investigate the association behavior of the Sn_{12}–oxo cluster macrocation $[(BuSn)_{12}O_{14}(OH)_6]^{2+}$ with two different and smaller anions, *p*-toluenesulfonate (PTS^-) and diphenylphosphinate ($Ph_2PO_2^-$). By monitoring the translational diffusion coefficients of the various species involved, it is shown that the association depends on the anion involved and on the solvent used. Moreover, the possibility to individually monitor the diffusion characteristics of multiple anionic and cationic species in mixtures, by virtue of resolved ^1H resonances available from each species, allows us to evidence the occurrence of ion exchange in such systems. Thus when $[(BuSn)_{12}O_{14}(OH)_6](PTS)_2$ is mixed with two equivalents of $Ph_2PO_2NMe_4$, PTS^- is displaced by $Ph_2PO_2^-$, highlighting the greater affinity of the organotin macrocation for the diphenylphosphinate. This example clearly illustrates the potential of pulsed field gradient ^1H NMR spectroscopy in inorganic/organometallic chemistry, to follow preferential ion pairing in multi-ion systems at the level of each individually charged species.

Keywords: cluster compounds • diffusion • ion pairs • NMR spectroscopy • tin

Introduction

Sn_{12}–oxo clusters of general formula $[(RSn)_{12}O_{14}(OH)_6]^{2+}$ are quasi-spherical macrocations, featuring a positive charge at each of the bowl shaped poles (see Figure 1).[1] Following their first description in 1989,[1a] several synthesis approaches have been reported in which this macrocation is prepared with different counterions.[1]

Sn_{12}–oxo clusters can be used as nanobuilding blocks for the synthesis of model hybrid organic–inorganic materials, in which telechelic dianions (e.g., α,ω-carboxyterminated polyethyleneglycol) or functional anions (e.g., 2-acrylamido-2-methyl-1-propanesulfonate) are used to assemble these nanobuilding blocks through electrostatic interactions.[2] Recently, they have also been shown to be fairly efficient and highly selective acetylation catalysts for alcohols, a behavior that has been related to their cationic character.[3] For both application areas (catalysis and hybrid materials), the presence of a charged species or of a tight ion pair with a specific anionic ligand is important and, concurrently, the availability of techniques to probe the ionic dissociation/association behavior of such species in solution is a prerequisite towards the tailored modulation of their properties.

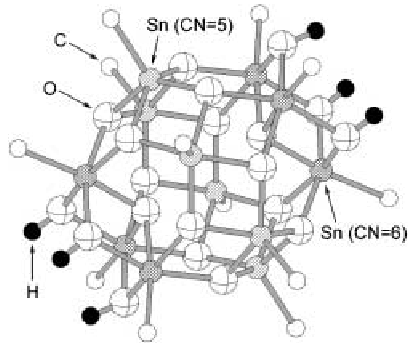

Figure 1. Molecular structure of the macrocation $[(BuSn)_{12}O_{14}(OH)_6]^{2+}$ (only the first carbon atom of each butyl chain has been drawn for clarity).

^{119}Sn NMR spectroscopy monitoring failed to provide any clear trends between the ^{119}Sn chemical shift and the extent of ionic dissociation/association. Indeed, the anions do not

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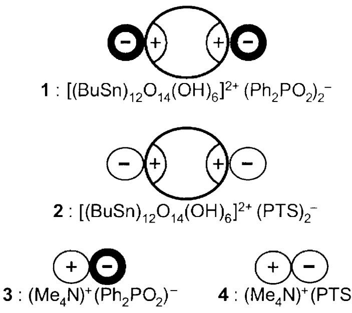
DOI: 10.1002/chem.200305604

interact directly with any of the tin atoms, but only through the μ_2-OH groups that define the positively charged poles of the cluster (see Figure 1). Therefore, in previous research, more elaborate NMR experiments (^{1}H,^{1}H NOESY and ROESY or ^{31}P,^{1}H HOESY) were needed to get insight into this issue.[1d,e] These studies have shown that in solvents with low dielectric constant (e.g., C_6D_6 or CD_2Cl_2), $[(BuSn)_{12}O_{14}(OH)_6]X_2$ (**1**: $X = Ph_2PO_2^-$ or **2**: $X = PTS^-$, Scheme 1) does not dissociate and the anions remain in close contact with the positive cluster poles, at which the anion–macrocation interaction also involves hydrogen bonds. In more dissociating solvents (e.g. [D$_6$]DMSO or C_6D_6/[D$_6$]DMSO 50:50), **2** was shown to dissociate, while **1** remains assembled as 1:2 macrocation–anion complex, even though the diphenylphosphinates appear slightly displaced away from the cluster poles.[1d,e] The ionic dissociation of **2** in DMSO was also confirmed by conductivity measurements.[1e]



Scheme 1. Ion triplets/pairs involved in the present work.

Pulsed field gradient (PFG) NMR spectroscopy is a very effective tool to study the translational motion of molecules and provides an elegant way to measure diffusion coefficients, even for mixtures of different structural units.[4,5] Its application is continuously expanding in bio-NMR spectroscopy and mixture analysis,[6] but has only lately started to emerge as a powerful tool in organometallic chemistry,[7] where, among other applications, it has provided evidence of ion pairing,[7b–i] self-assembly,[7j] aggregation,[7k] oligomerization of reactive intermediates,[7l] and speciation of aqueous silicates.[7m]

In the present case, diffusion coefficients should be very useful indicators of the extent of ionic association/dissociation, because the radius of the Sn$_{12}$ macrocation ($r \approx 9$ Å) is about twice that of the anions ($Ph_2PO_2^-$: $r \approx 4.8$ Å, and PTS^-: $r \approx 4.3$ Å).[8,9] Indeed, for globular molecules, the diffusion coefficient can be estimated by the Stokes–Einstein relation, $D = k_BT/6\pi\eta r_H$,[10] in which k_B is the Boltzmann constant, T is the absolute temperature (in Kelvin), η is the viscosity of the medium, and r_H is the hydrodynamic radius (i.e., the size of the moving entity that can include a crown of solvent molecules). Accordingly, if the macrocation is binding its two counterions, the same diffusion coefficients are expected to be obtained from fitting the diffusion-dependent attenuation of the ^{1}H resonances of the macrocation (butyl chains) and of the anions (phenyl ring protons for $Ph_2PO_2^-$, and phenyl ring and methyl protons for PTS^-). Conversely, if the macrocation and its anions are dissociated and surrounded by their own solvation shell, significantly different diffusion coefficients are expected for the macrocation and the anions, the diffusion coefficient being smaller for the macrocation than for its free anions. PFG-NMR spectroscopy was therefore used in order to investigate the ionic association/dissociation behavior of two pure Sn$_{12}$ based compounds, **1** and **2**, and to evidence possible ionic interchanges when they are mixed with other ion pairs.

Results and Discussion

The diffusion coefficients for the oppositely charged structural units that make up the ion pairs in **1**, **2**, $[NMe_4]^+ Ph_2PO_2^-$ (**3**) and $[NMe_4]^+PTS^-$ (**4**) (see Scheme 1), as well as for the **1+4** and **2+3** mixtures (in a 1:2 ratio), were measured in various solvents: C_6D_6, C_6D_6+[D$_6$]DMSO (85:15 v:v), C_6D_6+[D$_6$]DMSO (15:85 v:v), and [D$_6$]DMSO. Not all the compound/solvent combinations were investigated, either because they could not be achieved for solubility reasons (e.g. **1** is not soluble in pure [D$_6$]DMSO) or they were not expected to be relevant to the present study. According to the dielectric constant of benzene ($\varepsilon_r = 2.3$) and DMSO ($\varepsilon_r = 46.6$),[11] and also due to their strongly different abilities to solvate ions and generate hydrogen bonds, varying the solvent composition allowed us to modulate the dissociative behavior. Results are gathered in Table 1.

Because of the variation of the viscosity in these solvent mixtures (0.60 and 1.99 cP for benzene and DMSO, respectively)[12] and possible changes in the interactions with the medium, comparing the diffusion coefficients of a given species in different media is not straightforward. This difficulty can be alleviated by the addition in each mixture of a neutral nonpolarizable, and, therefore, noninteracting molecule, like tetramethylsilane (TMS); this which enables us to probe the variation of the local viscosity as a function of solvent composition.[13] Indeed, as expected from the Stokes–Einstein relation, the ratio of the diffusion coefficients of TMS in C_6D_6 and [D$_6$]DMSO (19.1/6.1 = 3.1) agrees well with the inverse ratio of the viscosities (1.99/0.60 = 3.3). However, such a comparison between different solvents is not essential to probe ionic association/dissociation, which can be assessed from the diffusion coefficients measured within a single experiment involving only one solvent or one solvent mixture.

Assuming full dissociation for **3** and **4** in [D$_6$]DMSO, the Stokes–Einstein relation can be used to estimate the hydrodynamic radii of $Ph_2PO_2^-$ and PTS^-. The calculated values, which amount to 3.6 and 3.0 Å, respectively, are smaller than those estimated from their spherical geometry.[9] These underestimations arise from the well-known limitation of the Stokes–Einstein relation when dealing with molecules smaller than about five times the size of the solvent molecules.[10] The diffusion coefficient of 1.2×10^{-10} m^{2}s^{-1} obtained for the Sn$_{12}$ macrocation in [D$_6$]DMSO corresponds to a hydrodynamic radius of 9.1 Å. For this larger and more spherically sized species, the Stokes–Einstein relation does hold and gives a good agreement with the estimated size of

Table 1. Diffusion coefficients ($\times 10^{-10}\,m^2 s^{-1}$) for **1**, **2**, **3**, **4**, **1+4** and **2+3** in various media.[a]

	Species	C_6D_6	C_6D_6/[D_6]DMSO (85/15)	C_6D_6/[D_6]DMSO (15/85)	[D_6]DMSO
1	$[BuSn_{12}]^{2+}$	4.2 ± 0.1	3.3 ± 0.1	1.5 ± 0.1	
	$Ph_2PO_2^-$	4.2 ± 0.1	3.3 ± 0.1	2.2 ± 0.1	
	TMS	19.3 ± 0.4	15.8 ± 0.2	7.1 ± 0.1	
2	$[BuSn_{12}]^{2+}$	4.0 ± 0.1	3.1 ± 0.1	1.6 ± 0.1	1.2 ± 0.1
	PTS^-	4.0 ± 0.1	3.2 ± 0.1	4.0 ± 0.2	3.4 ± 0.1
	TMS	19.1 ± 0.4	15.4 ± 0.3	7.3 ± 0.2	6.1 ± 0.1
3	Me_4N^+		5.4 ± 0.1	4.5 ± 0.1	3.9 ± 0.1
	$Ph_2PO_2^-$		5.3 ± 0.2	3.5 ± 0.1	3.0 ± 0.1
	TMS		15.9 ± 0.1	7.1 ± 0.1	6.2 ± 0.1
4	Me_4N^+		5.7 ± 0.1	4.5 ± 0.1	4.0 ± 0.1
	PTS^-		5.6 ± 0.1	4.2 ± 0.1	3.7 ± 0.1
	TMS		15.6 ± 0.4	7.3 ± 0.2	6.4 ± 0.3
1+4	$[BuSn_{12}]^{2+}$		3.2 ± 0.1 [3.3 ± 0.1]	1.5 ± 0.1 [1.3 ± 0.2]	
	$Ph_2PO_2^-$		3.3 ± 0.1 [3.4 ± 0.1]	2.4 ± 0.1 [2.3 ± 0.2]	
	PTS^-		5.5 ± 0.1 [5.6 ± 0.1]	4.1 ± 0.1 [3.8 ± 0.2]	
	Me_4N^+		5.6 ± 0.1 [5.9 ± 0.2]	4.5 ± 0.1 [4.2 ± 0.1]	
	TMS		15.6 ± 0.4 [16.1 ± 0.2]	7.1 ± 0.3 [6.4 ± 0.1]	
2+3	$[BuSn_{12}]^{2+}$		3.2 ± 0.1 [3.3 ± 0.1]	1.5 ± 0.1 [1.5 ± 0.1]	
	$Ph_2PO_2^-$		3.3 ± 0.1 [3.3 ± 0.1]	2.6 ± 0.1 [2.4 ± 0.2]	
	PTS^-		4.9 ± 0.1 [5.6 ± 0.1]	4.1 ± 0.1 [4.1 ± 0.1]	
	Me_4N^+		5.6 ± 0.1 [5.9 ± 0.2]	4.5 ± 0.1 [4.6 ± 0.1]	
	TMS		15.8 ± 0.3 [16.0 ± 0.2]	7.1 ± 0.2 [7.2 ± 0.1]	

[a] The initial concentrations are 8 mmolL^{-1} for **1** and **2** and 16 mmolL^{-1} for **3** and **4**. Values between brackets for the mixtures **1+4** and **2+3** correspond to a fivefold dilution. The reported D values result from averages over 5 to 10 experiments, corresponding to 5 to 10 couples of optimized parameters (δ, Δ) and over all the resonances related to the species under investigation.

8.5 Å.[8] Interestingly, the diffusion of the anions, observed to be faster than expected from their size, reinforces the favorable prerequisites for such PFG-NMR experiments on the association/dissociation properties of the Sn_{12} macrocation and its counteranions.

For **1** and **2** dissolved in C_6D_6 or C_6D_6+[D_6]DMSO (85:15 v:v), the macrocation and its anions exhibit identical diffusion coefficients within experimental error. The same holds for Me_4N^+ and its counterions in **3** and **4** in the latter solvent. Moreover, in C_6D_6+[D_6]DMSO (85:15 v:v), the diffusion coefficient is significantly smaller for **1** and **2** than for **3** and **4** in the same medium. These features clearly confirm the presence of ion-pairing for **1** and **2**, as expected for such poorly dissociating solvent mixtures.[1d,e] When C_6D_6+[D_6]DMSO (15:85 v:v) is used as a solvent, **1** and **2** behave differently. For **2**, in which the anion has no basic character, ionic dissociation is now clearly observed as evidenced by the large difference in the diffusion coefficients between the macrocation and the anion. Moreover, the diffusion coefficients measured in this solvent for PTS^-, whether originating from **2** or **4**, are identical within experimental error; this demonstrates a very high ionic dissociation of **2** in this DMSO-rich medium. In contrast, for **1**, in which the $PhPO_2^-$ ions correspond to a weak base, the ionic dissociation appears only partial in C_6D_6+[D_6]DMSO (15:85 v:v). The diffusion coefficient measured for the phosphinate anions originating from **1** is intermediate between that of the macrocation and that of the phosphinate anions originating from **3**. Assuming a fast association/dissociation equilibrium, as justified by the observed monogaussian damping of the signal amplitude, the measured diffusion coefficient is simply the arithmetic mean of the diffusion coefficients of the bound and free anions weighted by their respective molar fraction, that is, $\langle D \rangle = x_{free}D_{free} + (1-x_{free})D_{bound}$.[14] Taking the diffusion coefficient of the phosphinate measured for **3** in C_6D_6+[D_6]DMSO (15:85 v:v), $3.5 \times 10^{-10}\,m^2 s^{-1}$, as the lower limit of D_{free}, the degree of dissociation for **1** in such a medium is estimated to be no larger than 35%.

As ^1H NMR spectroscopy quite generally allows the various species present in solution to be discriminated through resolved ^1H resonances, species specific diffusion analysis by PFG NMR spectroscopy can be as easily performed in systems in which two anion/cation pairs are mixed up. This allows to study the behavior of the tin nanocluster when exposed to both counteranions in solution. Thus, when **1** and **4** are mixed in a 1:2 ratio in C_6D_6+[D_6]DMSO (85:15 v:v), the diffusion coefficients of the various species present are identical to those observed for **1** and **4** separately, indicating that no ionic interchange takes place. By contrast, the diffusion coefficients for the anionic species obtained after mixing **2** and **3** in the same solvent are very different from those observed for **2** and **3** separately, but very similar to those obtained for the mixture of **1** and **4**. This feature evidences that an ionic interchange is taking place, whereby the PTS^- in **2** is displaced from the cluster poles by the diphenylphosphinate anion, even though **2** alone is not dissociated in the same medium. The much stronger interaction of the phosphinate anion with the Sn_{12} cluster relative to that of the *p*-toluenesulfonate anion is hereby clearly demonstrated. However, notwithstanding this strong interaction, the PTS^- ion also appears to display a slightly lower diffusion coefficient in **2+3** relative to **1+4**. This indicates an interaction between a fraction of the PTS^- ion and **1**, while Me_4N^+ diffuses more freely. Fivefold dilution removes this surprising effect, in line with dilution idealizing solutions and, hence, inducing disaggregation of interacting moieties. In the DMSO-richer medium C_6D_6+[D_6]DMSO (15:85 v:v), the diffusion characteristics of all species in **2+3** are essentially pairwise identical within experimental error to those observed for **1+4**, confirming again that the phosphinate interacts more strongly with the macrocation than the sulphonate. It should be outlined, however, that there is a trend towards a slightly faster diffusion of the phosphinate anion in these mixtures **1+4** and **2+3** with respect to pure **1**, probably because of the higher amount of ions present.

Conclusion

By measuring the translational diffusion coefficients of the Sn$_{12}$–oxo cluster $[(RSn)_{12}O_{14}(OH)_6]X_2$ with PFG ^{1}H NMR spectroscopy, we have been able to probe its ionic dissociation/association behavior. More importantly, however, the possibility to monitor the association/dissociation behavior of the individual charged species in multi-ion mixtures has been demonstrated. Thus, ion exchange at the cluster's poles, governed by differences in binding affinities, have been identified and characterized qualitatively. To the best of our knowledge this is the first example that demonstrates the possibility to investigate preferential ion pairing in such multi-ion systems in inorganic/organometallic chemistry. It should be noted that compared to other techniques used in this respect, such as colligative methods or ionic conductivity measurements, it provides an unprecedented level of molecular speciation of such interactions in mixtures.

The availability of such information strongly contributes to a better understanding of the catalytic behavior of charged organotin–oxo clusters,[3] or to a better control of the "ionic" functionalization of these macrocations and their use as nanobuilding blocks in hybrid organic–inorganic materials.[2]

While the present study was performed on the special case of organotin–oxo clusters, the methodology can be considered as quite general and should be applicable to any type of charged metal–oxo cluster, provided that the cations and anions exhibit sufficiently different sizes for their diffusion coefficients to be unambiguously distinguished when they are dissociated. Finally, it is interesting to note that the electrostatic and hydrogen-bond-mediated interactions between the anions and the μ_2-OH defining the poles of such clusters are similar to those that could occur at the surface of oxide colloidal particles.[15] The recent availability of much stronger gradients (1100 $G\,cm^{-1}$ instead of 50 $G\,cm^{-1}$) opens a land of opportunity to study such association/dissociation phenomena at the surface of nanoparticles (5–50 nm), which are much larger than these oxo clusters. This should be applicable not only to charged species, but also to complexing organic ligands. The determinant condition to be fulfilled is having available an appropriate NMR nucleus with a sufficiently narrow resonance, a requirement that should be met when it is embedded in a rotationally mobile part of a suitable ligand interacting at the surface of the particle.

Experimental Section

Synthesis: $[(BuSn)_{12}O_{14}(OH)_6](O_2PPh_2)_2$ (**1**) and $[(BuSn)_{12}O_{14}(OH)_6](PTS)_2$ (**2**) were prepared according to published procedures.[1d,e] $[N(CH_3)_4](O_2PPh_2)$ (**3**) was prepared by reacting stoichiometric amounts of $[N(CH_3)_4]OH{\cdot}5H_2O$ with Ph_2PO_2H in ethanol, evaporating the solvent under reduced pressure and drying the final solids at 60°C. $[N(CH_3)_4](PTS)$ (**4**) was purchased from Fluka. The purity of all the compounds was assessed by ^{1}H and ^{119}Sn NMR spectroscopy.

Pulsed field gradient ^{1}H NMR spectroscopy: Samples were prepared for spectroscopy by dissolving the appropriate amounts of compounds in 0.7 mL of solvent in order to obtain a 8 $mmol\,L^{-1}$ solution for **1**, **2** and a 16 $mmol\,L^{-1}$ solution for **3**, **4**. The same concentrations are used in the mixtures **1**+**4** and **2**+**3**, providing a 1:2 molar ratio of **1** or **2** to **3** or **4** in all cases.

Diffusion coefficients were measured by pulsed field-gradient (PFG) ^{1}H NMR spectroscopy by means of a BPP-LED pulse sequence.[16] Experiments were carried out at 298 K, without spinning and in the absence of any gas flow, enabling one to minimise convection artefacts by essentially eliminating all artificial sources of temperature gradients, on a Bruker Avance 250 spectrometer interfaced with a PC computer and equipped with a Bruker BGU z-gradient unit providing a maximum gradient of 53.5 $G\,cm^{-1}$. Preliminary 1D measurements, with an LED-bipolar gradient pulse pair program, were performed on each solution in order to optimize simultaneously the gradient pulse duration (δ) and the diffusion delay (Δ) so as to detect properly the full signal decay.[17] Selected measurements were also performed on a Bruker Avance 500 spectrometer, and yielded the same values within experimental error, indicating the reproducibility was independent from the instrument setup.

The amplitude of the gradients were varied from 2% to 95% of their maximum value, while the gradient recovery delay (τ) and the eddy current delay (T_e) were fixed at 0.2 ms and 5 ms, respectively. The diffusion delay (Δ) varied in the range 50–280 ms and the gradient pulse duration (δ) in the range 1–3.5 ms. Similar measurements with ^{119}Sn resonances were impossible because of the fast ^{119}Sn T_1 relaxation,[1e] which is incompatible with the diffusion delays (Δ) needed with regards to the maximum gradient strength available.

Acknowledgments

M.B., R.W., and J.C.M. are indebted to the Fund for Scientic Research Flanders (Belgium) (FWO, Grant G.0016.02) and to the Research Council of the VUB (Grant OZR 875) for financial support. V.E. is a postdoctoral fellow of the FWO (contract GP00703N). F.R. is indebted to the "Wetenschappelijke Onderzoeksgemeenschap van het FWO" "Gevorderde NMR toepassingen in de materiaal-, chemische en biomedische wetenschappen" (Grant WO.010.02N, 2002–2006) for a visiting scientist fellowship.

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[8] The size of $[(BuSn)_{12}O_{14}(OH)_6]^{2+}$ was estimated by two independent methods. According to the molecular structures determined by single-crystal X-ray diffraction,[1] a sphere of ~8.5 Å of radius contains the macrocation. ^{119}Sn T_1 measurements can also provide information on the hydrodynamic radius of the organotin–oxo clusters. Indeed for such species, the main ^{119}Sn relaxation mechanism is chemical shift anisotropy (CSA). T_{1CSA} can be related to the chemical shift anisotropy (ζ) and asymmetry (φ) as well as to the correlation time, which depends on the viscosity of the medium and on the hydrodynamic diameter through the Debye–Stokes–Einstein relation ($\tau_c = 4\pi\eta r_H^3/3k_BT$).[18] According to the T_1 values of **2** in CD_2Cl_2 (0.20 and 0.15 s for the six- and five-coordinate tin atoms, respectively)[1e] and to its ^{119}Sn chemical shift anisotropy parameters (ζ = 320 ppm, φ = 0.2 and ζ = 390 ppm, φ = 0.3 for the six- and five-coordinate tin atoms, respectively)[1e] as determined by ^{119}Sn MAS NMR spectroscopy, a hydrodynamic radius of 9.5 Å, which includes two bonded *p*-toluenesulfonates, can be computed for **2**.

[9] The size of $Ph_2PO_2^-$ and PTS^- was estimated from their molecular structures as the radius of the sphere centered on their geometrical center (r_G) or on their mass center (r_M) and which includes all the atoms. The values are $r_G = 4.75$, $r_M = 4.95$ Å for $Ph_2PO_2^-$ and $r_G = 3.8$, $r_M = 4.8$ Å for PTS^-. The large difference between r_G and r_M for PTS^- is linked to the clear disymmetry brought by the sulfonate group. However, for PTS^-, the elongated shape of the molecule makes the "globular" approximation less reasonable.

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Received: October 7, 2003 [F5604]