Coordination Mode and Kinetic Behavior of the Tetracarbonatozirconate Ion

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The behavior of $[Zr(CO_3)_4]^{4-}$ complex in solution is studied by determining the coordination mode of the carbonato ligands and the kinetic law of the equilibrium between free and complexed carbonates. *Raman* polarization and dynamic ^{13}C-NMR experiments show that complexed carbonates are bidentate. Magnetization-transfer experiments give the values of pseudo-first-order rate constants for the equilibrium with no net chemical transformation. The treatment of these parameters suggests a second-order rate law. As no solvent effect is noticed, an associative mechanism of ligand exchange is proposed.

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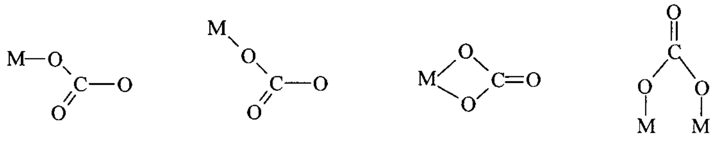
1. Introduction. – Current interest in the chemistry of zirconium in aqueous solution derives from the necessity of nuclear-waste repository. The aqueous-solution chemistry of this metal is dominated by hydroxo-complex formation [1–4]. In all natural media, carbonate ions are very abundant. As they are very good complexing agents, the knowledge of interactions between hydroxide and carbonate ions with zirconium is necessary to understand the metal's behavior in H_2O.

Most studies on zirconium have dealt with the formation of solid compounds [5–7], and the elaboration of complexes soluble in aqueous environments has received very little interest [8–10]. Studies about solid compounds are ancient and describe synthetic routes and analysis of hydroxocarbonate complexes. *Pospelova* and *Zaïtsev* [5] synthetized several complexes and determined their stoichiometry. The number of complexed carbonates per zirconium varies from one to four. The most carbonated solid species is $[Zr(CO_3)_4]^{4-}$. IR Studies [6] of this compound revealed that the four carbonato groups are bidentate. Some of other synthesized hydroxocarbonate complexes have bridging carbonato groups. It is, however, difficult to determine the carbonato coordination mode. *Clearfield* [7] analyzed the crystalline dinuclear complex $(NH_4)_6[Zr(CO_3)_3(OH)]_2 \cdot 4\ H_2O$ and concluded that it contains three bidentate carbonato ligands and hydroxo bridges between the metal cations, the Zr^{IV} ion having the coordination number eight. *Dervin et al.* [8] further examined the behavior of Zr^{IV} with carbonate ions in aqueous solution by several techniques like protometry, cryoscopy, conductimetry, and ion exchange, which revealed the formation of the complex ion $[Zr(CO_3)_4]^{4-}$. *Joao et al.* [9] studied $[Zr(CO_3)_4]^{4-}$ as well, but no structural investigation was carried out in solution. *Malinko et al.* [10] exploited potentiometric titrations of solutions containing carbonate and Zr^{IV} ions. Using the position of the equivalence points, these authors concluded that four complexes could be obtained, *i.e.*, $[ZrCO_3(OH)_3]^-$, $[Zr(CO_3)_2(OH)_2]^{2-}$, $[Zr(CO_3)_3(OH)]^{3-}$, and $[Zr(CO_3)_4]^{4-}$. These solution studies were qualitative and mainly established the stoichimetry of the hydroxocarbonate complexes.

The present study aims to investigate the structure of purely carbonated complexes of zirconium, *i.e.* $[Zr(CO_3)_4]^{4-}$, in a way that carbonatouranyl complexes have been studied for many years [11–16]. Thus, *Raman* and ^{13}C-NMR spectroscopy are used for the elucidation of the coordination mode of the carbonato ligands and of the kinetic behavior of $[Zr(CO_3)_4]^{4-}$.

2. Results. – 2.1. *Coordination Mode of Complexed Carbonate Ions.* 2.1.1. *Preamble. Raman* and NMR spectroscopy present the advantage of elucidating the coordination mode of complexed carbonate ions in solution. Four coordination modes are possible for this ligand (*Fig. 1*): monodentate C_s or C_{2v} (see **A** and **B**, resp.), bidentate C_{2v} (see **C**), or bridging C_{2v} (see **D**).



A monodentate C_s **B** monodentate C_{2v} **C** bidentate C_{2v} **D** μ_2-bridging C_{2v}

Fig. 1. *Coordination modes of the carbonate ion*

In the case of **A** and **B**, one O-atom of the carbonato ligand is involved in the complex formation, whereas in the case of **C** and **D**, two O-atoms are linked to Zr^{IV}. Partly for this reason, *Raman* spectroscopy allows us to distinguish essentially between monodentate and bidentate or bridging coordination modes. ^{13}C-NMR Spectroscopy provides additional information about the coordination mode.

2.1.2. Raman *Spectroscopy.* The free carbonate ion CO_3^{2-} belongs to the D_{3h} group, and has the following fundamental vibrations [17]: ν_1, symmetrical stretching vibration (active in *Raman* spectroscopy); ν_2, deformation vibration out of the plane (inactive in *Raman* spectroscopy); ν_3, asymmetrical stretching vibration (active in *Raman* spectroscopy); ν_4, deformation vibration in the plane (active in *Raman* spectroscopy).

The complexation and the protonation of carbonate ions cause a shift of the bands [17] and a decrease of symmetry, from the D_{3h} to C_s or C_{2v} groups. The four bands ν of the free carbonate ion are split into six bands ν', and the correspondence between D_{3h} and C_{2v} groups is as follows: $\nu_1 \rightarrow \nu'_2$, $\nu_2 \rightarrow \nu'_6$, $\nu_3 \rightarrow \nu'_1$ and ν'_4, $\nu_4 \rightarrow \nu'_3$ and ν'_5.

The $[Zr(CO_3)_4]^{4-}$ complex is always obtained in solution with an excess of hydrogencarbonate and carbonate ions. Consequently, some vibrations are superimposed. Four criteria [18] have been defined for distinguishing between the monodentate and bidentate modes, both belonging to C_{2v} groups [17]: *1*) The magnitude of frequency splitting of ν'_1 and ν'_4 vibrations is higher in a bidentate than in a monodentate structure. *2*) In the low-frequency region, bidentate structures have two coordination modes of A_1 and B_2 symmetries, whereas monodentate structures have only one with an A_1 symmetry.

3) The frequency difference of combination bands between $(\nu'_2+\nu'_4)$ and $(\nu'_2+\nu'_1)$ is higher in dicoordinate than in monocoordinate complexes. The frequency difference between $(\nu'_2+\nu'_3)$ and $(\nu'_2+\nu'_5)$ is equal to *ca.* 10 cm^{-1} for bidentate and 30 cm^{-1} for monodentate carbonates. *4*) According to *Taravel* [18], the following criterion is the most reliable for determination of the coordination mode of carbonate ions in solution. In complexes with monodentate carbonato ligands, the ν'_4 band of higher frequency (B_2 symmetry) is depolarized, whereas the ν'_1 band of lower frequency (A_1 symmetry) is polarized. In the case of complexes with bidentate carbonato ligands, symmetries and assignments are opposite. The depolarization factor ρ is equal to the ratio of band intensity of parallel polarization and of perpendicular polarization. If $0 \leq \rho < \rho_{max}$ (the ρ_{max} value is *ca.* 0.8 and depends on the metal center), the band is polarized. If $\rho = \rho_{max}$, the band is depolarized. For monodentate C_s-complexed carbonato ligands, all identified vibrations should be polarized.

Few studies have dealt with the determination of a bridging coordination mode. To our knowledge, only *Taravel* [18] proposes a criterion that distinguishes between bidentate and bridging carbonato ligands. The criterion concerns the number of bands for which the wavenumber is below 500 cm^{-1}. This number is equal to four for bridging and equal to two for bidentate ligands.

The system $[Zr(CO_3)_4]^{4-}$ presents some inherent problems when studied by *Raman* spectroscopy. A very broad line is centered at 324 cm^{-1}, with a width of 80 cm^{-1}. This band certainly includes or masks other vibrations. Thus, the wavenumber domain below 500 cm^{-1} cannot be studied, and the second and fourth criteria mentioned above can not be exploited. The third criterion deals with recombination bands. However, in solution, the *Raman* spectroscopy is not sensitive enough to identify these bands. Furthermore, the quoted theoretical values depend on the strength of the metal–O bond, so the first and third criteria are not reliable. The fourth criterion is the only one which can be exploited with reliability. For polarization experiments, D_2O is employed as solvent instead of H_2O because the band at 1680 cm^{-1} is only a shoulder of the ν_2 deformation vibration of H_2O. *Fig. 2* presents the superimposition of the spectra of a solution containing $[Zr(CO_3)_4]^{4-}$, K_2CO_3, and $KHCO_3$ in parallel and perpendicular polarizations between 1250 and 1750 cm^{-1}. The two high-intensity bands of the spectrum in parallel polarization, at 1640 and 1360 cm^{-1}, correspond to the ν_2 deformation vibration of H_2O (arising from the initial product $ZrOCl_2 \cdot 8\ H_2O$) and to the ν_3 vibration of the hydrogencarbonate ion, respectively [11]; both are polarized. The two low-intensity bands, at 1680 and 1300 cm^{-1}, correspond to the splitting of the ν_3 doubly degenerate vibration of free carbonate ions. The one of higher energy with a depolarization factor of 0.1 is polarized and corresponds to the ν'_1 vibration. The other one with a depolarization factor of 0.9 is depolarized and corresponds to the ν'_4 vibration. From the comparison of the *Raman* spectrum of a solution containing the complex with carbonate and hydrogencarbonate ions (concentrations at equilibrium: $[Zr(CO_3)_4{}^{4-}] = [CO_3{}^{2-}] = [HCO_3{}^{-}] = 0.3\text{M}$) with the one of a solution of carbonates ($[CO_3{}^{2-}] = [HCO_3{}^{-}] = 0.3\text{M}$), the *Raman* vibrations of complexed carbonates of $[Zr(CO_3)_4]^{4-}$ can be assigned as follows: ν'_1 (A_1) 1680(sh), ν'_2 (A_1) 1048*s* (br.), ν'_3 (A_1) 790*w*, ν'_4 (B_2) 1300*w*, and ν'_5 (B_2) 750*w* cm^{-1}, ν'_6 (B_1) being inactive. These results establish that complexed carbonates are of symmetry C_{2v}, and their coordination modes can only be bidentate or μ_2-bridging [18].

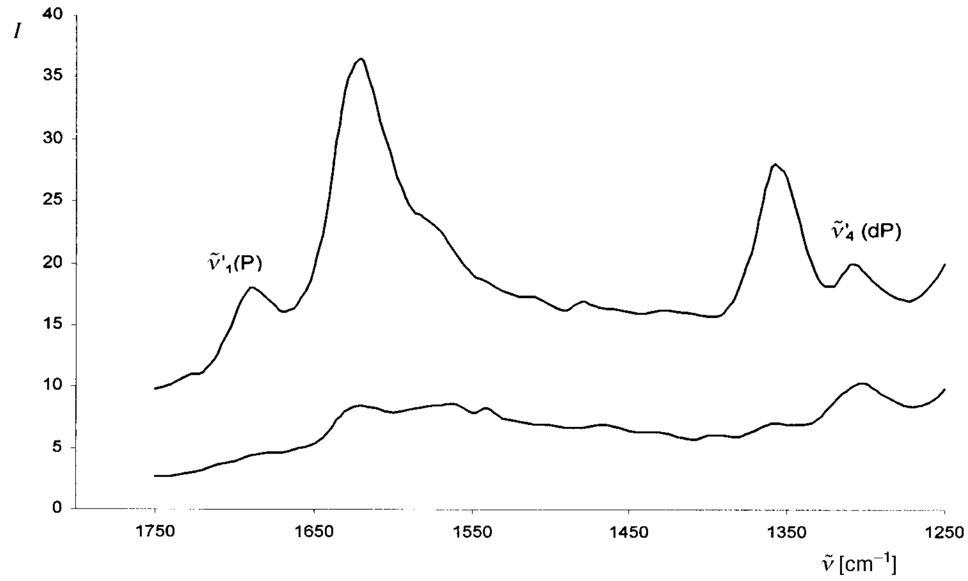


Fig. 2. *Polarized* Raman *spectra of a solution of* $[Zr(CO_3)_4]^{4-}$, K_2CO_3, *and* $KDCO_3$ *in* D_2O $[[Zr(CO_3)_4]^{4-}] = 0.15$M, $[K_2CO_3] = 0.15$M, $[KDCO_3] = 0.15$M. Upper trace, parallel polarization; lower spectrum trace, perpendicular polarization; *I*, emission intensity in arbitrary units.

2.1.3. *^{13}C-NMR Spectroscopy.* As *Raman* spectroscopy does not distinguish between a bidentate or bridging coordination mode, ^{13}C-NMR spectroscopy is used to resolve this last ambiguity. Separately recorded spectra of carbonate and hydrogencarbonate solutions show chemical shifts δ at 168.6 and 161, respectively, for the ionic strengths of 1 and 2 $\text{mol} \cdot \text{l}^{-1}$ in KNO_3 media. A typical spectrum of a mixture of carbonate and hydrogencarbonate ions exhibits only one peak, with an average δ value that depends on the pH, due to the fast proton exchange between the two species.

Fig. 3 shows the ^{13}C-NMR spectrum of the $[Zr(CO_3)_4]^{4-}$ complex in solution with carbonates. The two peaks observed at δ_1 and δ_2 arise from the complexed carbonates of $[Zr(CO_3)_4]^{4-}$ and the free carbonates, respectively, the latter including carbonate and hydrogencarbonate ions, and the δ values are assigned by comparison with those of other samples in which the initial composition of the solution is different. The chemical-shift value of the complexed carbonates, which is always 168.3 ppm, is close to the chemical-shift value of free carbonates (168.6). The same fact has already been observed for complexed carbonates of $[UO_2(CO_3)_3]^{4-}$ (δ 168.9) and uncomplexed carbonates (δ 169.6) [12]. These observations show that only carbonate ions are involved in the complexation of Zr^{IV}, and that metal-cation binding only slightly affects the δ of the carbonato ligands. The studies of the carbonate/uranyl system reveal two dominating carbonato complexes, *i.e.*, $[UO_2(CO_3)_3]^{4-}$ and $[(UO_2)_3(CO_3)_6]^{6-}$, the former having three bidentate carbonato ligands and the latter three bidentate and three μ_3-bridging carbonato ligands [12] [13] [15] [16] [19] (the small variations in the δ values reported for the same carbonato complexes arise from different NMR-recording conditions).

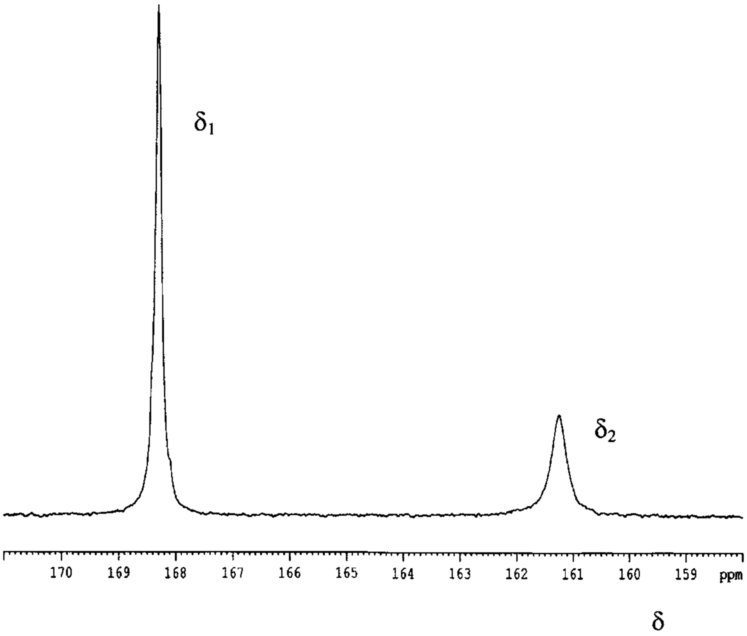


Fig. 3. *^{13}C-NMR Spectrum of a solution containing $[Zr(CO_3)_4]^{4-}$ and free carbonate.* [$[Zr(CO_3)_4]^{4-}$ = 0.09M, [Na_2CO_3] = 0.02M, [$NaHCO_3$] = 0.18M.

The bidentate carbonato ligand of the mononuclear and trinuclear uranyl species gives rise to δ 170.10 and 170.27, respectively [16]. When both species are mixed, the δ values of these bidentate carbonato ligands can be resolved only at low temperature. The μ_3-bridging carbonato ligand of the trinuclear species appears at δ 171.42. When the carbonato coordination mode is different, their δ values differ significantly. Unfortunately, to our knowledge, no NMR study of Zr complexes in aqueous solution has been carried out; thus, the δ_1 values do not allow us to differentiate among coordination modes. Experimental dynamic NMR data are needed for this purpose (see *Sect. 2.2*).

To evaluate the rate of the exchange between free carbonates and complexed carbonates of $[Zr(CO_3)_4]^{4-}$, magnetization-transfer experiments are carried out for series of solutions in which the zirconium(IV) concentration varies from 0.05 to 0.09M. During these experiments, one of the two sites involved in the exchange is selectively irradiated. The kinetic data obtained are the pseudo-first-order rate constants k_{obs}, which are deduced from the time dependence of the intensity of the signal of the unperturbed site. The pseudo-first-order rate constant k_{obs}^{12} characterizes the rate of moving from the site of complexed carbonates to the site of free carbonates, and k_{obs}^{21} describes the opposite move. Their values depend on experimental conditions like the concentration of the metal cation. The k_{obs}^{12} values obtained for the $[Zr(CO_3)_4]^{4-}$ system vary between 21.3 and 87.7 s^{-1}. These results are compared with those of a similar study of the free and complexed carbonates of $[(UO_2)_3(CO_3)_6]^{6-}$, where the bidentate carbonato ligands are in chemical exchange with free carbonates in solution, and μ_3-bridging carbonato ligands do not exchange with free carbonates; for this system, the pseudo-first-order rate constant k^{12}_{obs} is 42 s^{-1} for bidentate carbonato and free carbonate exchange in 0.237 and 0.1M metal cation solutions. Thus, bidentate carbonato ligands of $[(UO_2)_3(CO_3)_6]^{6-}$ have similar dynamic characteristics as complexed carbonates of $[Zr(CO_3)_4]^{4-}$, both being in chemical exchange with free carbonates exhibiting pseudo-first-order rate constants k^{12}_{obs} of the same order of magnitude. Thus, complexed carbonates of $[Zr(CO_3)_4]^{4-}$ cannot be bridged. *Raman* and ^{13}C-NMR investigations establish unambiguously that carbonate ions of $[Zr(CO_3)_4]^{4-}$ are bidentate.

2.2. *Equilibrium Dynamics of Complex Ion* $[Zr(CO_3)_4]^{4-}$. 2.2.1. *Pseudo-first-order Rate Constants.* To determine the rate law of the chemical exchange between the free and complexed carbonates of $[Zr(CO_3)_4]^{4-}$, the corresponding pseudo-first-order constants are determined and then the kinetic constants calculated.

The presence of both peaks in the ^{13}C-NMR spectrum (*Fig. 3*) indicates a slow exchange between free and complexed carbonates on the NMR scale. The broadening of the resonances depends on the exchange rate, the transverse relaxation time, and the inhomogeneity of the magnetic field. If the band-width is of the same order of magnitude as the broadening due to the inhomogeneity of the magnetic field, no kinetic information can be deduced by band-shape analysis. The line-widths of the resonances of the complexed and free carbonates vary between 10 and 30 Hz. These small broadenings do not allow the application of band-shape analysis, *i.e.*, the chemical exchange is too slow. Thus, the pseudo-first-order rate constants are obtained from magnetization-transfer experiments (*Fig. 4*). To evaluate partial orders, two series of experiments are carried out, one at constant complex concentration and the other at constant hydrogencarbonate and carbonate ion concentration. The $[Zr(CO_3)_4]^{4-}$ complex formation occurs according to *Eqn. 1.*

The stoichiometry of the studied complex is confirmed by the quantitative analysis of the ^{13}C-NMR spectra, which reveal the presence of four complexed carbonate ions

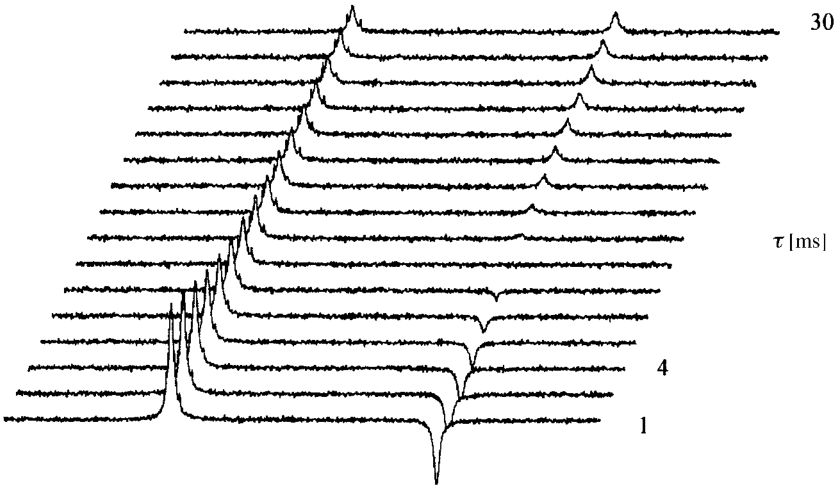


Fig. 4. *^{13}C-NMR, selective magnetization transfer between free and complexed carbonate sites.* The numbers represent the delay τ [ms] between the selective inversion π-pulse and the read pulse. $[[Zr(CO_3)_4]^{4-}] = 0.07$M, $[Na_2CO_3] = 0.02$M, $[NaHCO_3] = 0.28$M.

per Zr^{IV} atom. Then the ratio hydrogencarbonate ions/carbonate ions, present in solution after the complex formation, is evaluated. This ratio is equal to $(y-2)/(x-2)$. After complex formation, there is a large excess of hydrogencarbonate ions in all studied solutions. So 'free carbonates' means that mainly hydrogencarbonate ions participate in the exchange equilibrium.

The variations of k^{12}_{obs} and k^{21}_{obs} *vs.* the free hydrogencarbonate-ion concentration and the complex concentration are plotted in *Figs. 5* and *6*, respectively.

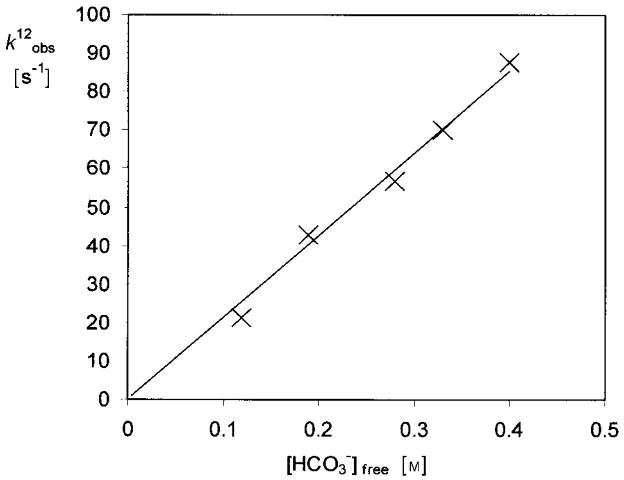


Fig. 5. *Pseudo-first-order rate constant* k^{12}_{obs} vs. *concentration of the free hydrogencarbonate ion.* Constant Zr^{IV} concentration $= 0.07$M; k^{12}_{obs}, x.

$$[Zr(OH)_2]^{2+} + x\ CO_3^{2-} + y\ HCO_3^- \rightarrow [Zr(CO_3)_4]^{4-} + (x-2)\ CO_3^{2-} + (y-2)\ HCO_3^- + H_2O \tag{1}$$

2.2.2. *Determination of the Rate Equations.* The k^{12}_{obs} values show a linear dependence on the free hydrogencarbonate-ion concentration and are not dependent on the complex concentration. The k^{21}_{obs} values exhibit the opposite dependence (*Figs. 5* and *6*) from which the following exchange path can be deduced. As noticed, there is no net chemical transformation in this equilibrium (*Eqn. 2*).

From the linear plots k^{12}_{obs} *vs.* hydrogencarbonate concentration and k^{21}_{obs} *vs.* complex concentration, the following second-order rate constants are determined: $k^{12} = 214 \pm 14\ \mathrm{M}^{-1} \cdot \mathrm{s}^{-1}$ and $k^{21} = 838 \pm 20\ \mathrm{M}^{-1} \cdot \mathrm{s}^{-1}$. Since one molecule of $[Zr(CO_3)_4]^{4-}$ contains four CO_3^{2-} ligands, we obtain *Eqn. 3.* As kinetic rates are equal in both directions, it follows that $k_{21} = 4 \cdot k_{12}$, in agreement with the experimental findings.

$$[Zr(^*CO_3)_4]^{4-} + HCO_3^- \underset{k^{21}}{\overset{k^{12}}{\rightleftharpoons}} [Zr(CO_3)_4]^{4-} + H^*CO_3^- \tag{2}$$

$$\begin{aligned} \text{rate} &= d[HCO_3^-]/dt = k^{21} \cdot [HCO_3^-] \cdot [[Zr(CO_3)_4]^{4-}] \\ &= -1/4\ d[Zr(CO_3)_4^{4-}]/dt = k^{12} \cdot \mathbf{4} \cdot [[Zr(CO_3)_4]^{4-}] \cdot [HCO_3^-] \end{aligned} \tag{3}$$

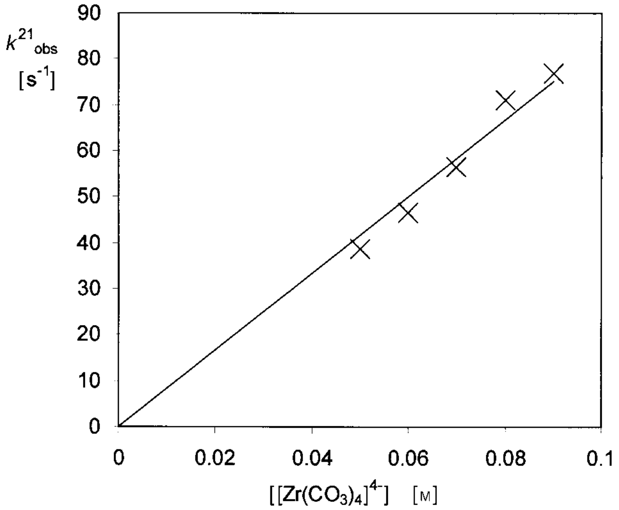


Fig. 6. *Pseudo-first-order rate constant* k^{21}_{obs} vs. *concentration of the zirconium complex.* Constant hydrogencarbonate/carbonate concentration = 0.56M; k^{21}_{obs}, x.

In these experiments, the pH does not vary sufficiently to determine any dependence of k_{obs} on pH. The difference of pH between the various solutions is at most 0.8. If the pH increases or decreases more, the $[Zr(CO_3)_4]^{4-}$ complex is no longer present in the solution. No temperature-dependence experiments can be carried out since the $[Zr(CO_3)_4]^{4-}$ complex undergoes hydrolysis on heating. Therefore, no thermodynamical data, such as entropy and enthalpy, can be determined.

3. Discussion.

– Our results establish that carbonato ligands in the soluble $[Zr(CO_3)_4]^{4-}$ complex are bidentate. The rate law of the chemical exchange between free and complexed carbonates has been determined. During dynamic NMR studies of the $[UO_2(CO_3)_3]^{4-}$ and $[(UO_2)_3(CO_3)_6]^{6-}$ complexes, *Banyai et al.* [16] noticed a clear correlation between the kinetic behavior and the coordination mode of the carbonato ligands. Only dynamic NMR studies allow examination of the actual reaction mechanism in solution. There are four possibilities for the exchange mechanism between complexed and free carbonates. It can be associative (A), dissociative (D), interchange associative (Ia), or interchange dissociative (Id) [20]. The rate-determining step is the breaking or the formation of the $Zr^{IV}-CO_3^{2-}$ bond in the cases of a dissociative or associative process, respectively. The mechanism identification relies on the rate-limiting-step determination.

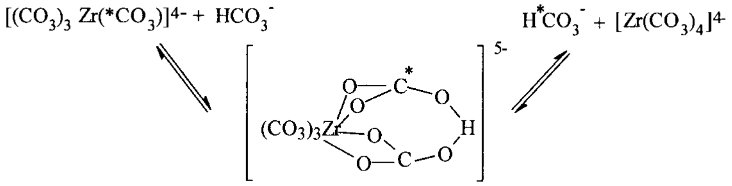
As four bidentate carbonates per zirconium are complexed, the maximum coordination number of Zr^{IV} is reached. The identified rate law shows a straightforward bimolecular route. We could assume that the mechanism implies a limit pathway, being either associative or dissociative. The reaction intermediate should be identified to determine if the rate-determining step is the formation or the breaking of the metal-carbonato bond. To evaluate the strength of this bond, the ligand-substitution reaction of *Eqn. 4*, in which the rate-determining step is the dissociation of the carbonate ion

[15], should be tested. Unfortunately, no ligand that makes this reaction thermodynamically favorable seems to be known.

$$[Zr(CO_3)_4]^{4-} + L^{n-} \rightleftharpoons [Zr(CO_3)_3L]^{(n+2)-} + CO_3^{2-} \qquad (4)$$

To evaluate the solvent effect, solutions with similar initial composition but containing a different percentage of D_2O are compared. The ratios of the pseudo-first-order rate constants k^{12}_{obs} (20% D_2O)/k^{12}_{obs} (86% D_2O) is 1.1 and that of k^{21}_{obs} (20% D_2O)/k^{21}_{obs} (86% D_2O) is 1.2. The pseudo-first-order rate-constant values do not vary significantly enough in the two solvent systems to suspect a participation of water or proton in the reaction mechanism. In the case of a pure dissociative mechanism, the reaction intermediate would be $[Zr(CO_3)_3]^{2-}$, and one may expect a competition between solvent and ligand molecules to bind to Zr^{IV}. In such a case, a solvent effect would occur. On account of the lack of a solvent effect, the most probable mechanism seems to be rather associative, and the rate-determining step is the formation of the $Zr-CO_3{}^{2-}$ bond. According to *van Eldik* [20], an associative mechanism would lead to a reaction intermediate with an increased coordination number, *i. e.*, in the present case to $[Zr(CO_3)_5]^{6-}$. Unfortunately, the signs of thermodynamical data, such as the activation entropy and the activation volume of the reaction, which are very useful to determine the mechanism type [20], cannot be determined for the $[Zr(CO_3)_4]^{4-}$ system (see *Sect. 2.2.2.*). Finally, in analogy to the Tl-CN^- system [21], we propose the exchange mechanism shown in the *Scheme.* However, the identification of the reaction intermediate is not sufficient for an accurate description of the mechanism, because many different steps with rearrangement of species could occur. Another possible mechanism would be a shift of the carbonate from a bidentate binding mode to a monocoordination mode; this could explain the very slightly different rates in H_2O and D_2O, and the coordination number of eight would be respected.

Scheme. *Reaction Intermediate*



4. Conclusion. – The environment of the metal cation in the $[Zr(CO_3)_4]^{4-}$ complex in solution is established. The four carbonato ligands are bidentate as in the solid state, which is consistent with a mononuclear structure. The ^{13}C-NMR chemical shift of this type of complexed carbonates can now be used as a reference in aqueous Zr^{IV} chemistry. In an upcoming publication, this chemical shift will be compared to other chemical shifts of hydroxocarbonato complexes of Zr^{IV}. Referring to other similar studies with carbonato uranyl complexes, the relation between the carbonato coordination mode and the kinetic behavior of carbonato complexes is disclosed. The pseudo-first-order rate-constant values for the exchange between bidentate and free carbonates of $[Zr(CO_3)_4]^{4-}$ and $[(UO_2)_3(CO_3)_6]^{6-}$ in solution are of the same order of magnitude [16].

Despite the lack of thermodynamical data, an associative mechanism with no net chemical transformation is proposed for the exchange reaction studied. The exchange reaction between complexed and free carbonates of $[Zr(CO_3)_4]^{4-}$ is compared with that of $[UO_2(CO_3)_3]^{4-}$. This latter complex also contains only bidentate carbonato ligands but involves a dissociative mechanism [15]. So, even for a similar carbonato coordination mode, the type of mechanism depends on the metal cation.

Experimental Part

1. General. Raman and NMR studies require high ligand and zirconium(IV) concentrations. Ionic strength: 1.2–1.5M for NMR solns. and *ca.* 4M for *Raman* solns., without further addition of KNO_3.

2. Raman *Spectroscopy.* Tetracarbonatozirconium(IV) solns. are prepared using the following conditions: a known volume of 2M K_2CO_3 and a known volume of 2M $KHCO_3$ are mixed. A calculated volume of $ZrOCl_2 \cdot 8\ H_2O$ at the desired concentration is added dropwise under vigorous stirring to avoid local precipitation of zirconium hydroxide.

Zr^{IV} Concentration, 0.15–0.30M; total carbonate concentration, *i.e.*, carbonate and hydrogencarbonate concentration, 0.9–1.8M; carbonate and hydrogencarbonate ions/zirconium, at least 6 to allow the formation of $[Zr(CO_3)_4]^{4-}$. Laser *Raman* measurements: *OMARS 89* model spectrometer (*Dilor*, France); grating blazed at 1800 grooves/mm as monochromator; signal detection with a *CCD* apparatus (512 pixels), spatial resolution *ca.* 4 cm^{-1}, excitation by the 514.5-nm line of an Ar^+ laser (model *2017, Spectra Physics*) operating at 800 mW and 1200 mW.

3. ^{13}C-NMR Spectroscopy. The CCl_4 solns. are prepared using the above method, except that 1M carbonate and 0.92M hydrogencarbonate solns. with 100% ^{13}C isotopic enrichment are used (from *Sigma-Aldrich*). Solvent composition, H_2O/D_2O 80:20, diameter of the NMR tubes, 5 mm. Total concentration of Zr^{IV}, 0.05–0.09M; total carbonate concentration, always higher than 5 times the Zr^{IV} concentration. ^{13}C-NMR Measurements: chemical shifts δ in ppm with respect to the central line of external CD_3OD, calibrated at 49.02 ppm; *Bruker-DRX-500* spectrometer (at 125.77 MHz for ^{13}C). As no heteronuclear NOE or scalar coupling is expected, the spectrum in *Fig. 3* is recorded using the simple delay (30 s) – pulse (6 µs, 60 degrees) – acquisition (406 ms, 4K points) pulse program (zg), 8 scans being sufficient to provide a convenient signal-to-noise ratio. The longitudinal relaxation time T_1 is measured for solns. of ligands without and with metal cation by using the well-known inversion-recovery method [22]: T_1 30 s (CO_3^{2-} soln.), 9 s (HCO_3^- soln.), 7 s (CO_3^{2-}/HCO_3^- 1:1 soln.), and 15 s ($[Zr(CO_3)_4]^{4-}$ soln., in equilibrium with HCO_3^- and CO_3^{2-}; averaged value for the present species in soln.). The number of linked carbonate/Zr^{IV} is checked by measuring the integrals of the free and complexed carbonate NMR signals.

4. Magnetization Transfer Experiments [23]. *Cf. Sect. 3.* The inversion DANTE pulse train is made of pulses (10 µs) and delays (50 µs) resulting in an overall 3-ms duration (*Fig. 7*), length of the read pulse 6 µs; gradient pulses, sine-arch modulated with a maximum intensity of 5 and 12.5 cm^{-1} for G_1 and G_2, resp., lasting 2 ms and

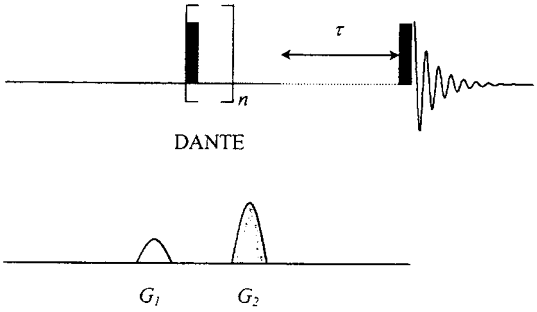


Fig. 7. *Pulse sequence used in the magnetization-transfer experiment*

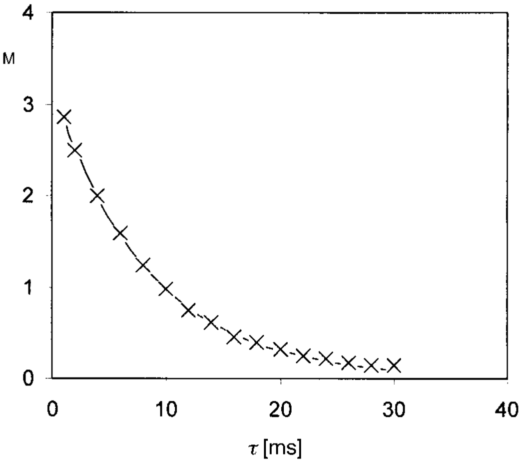


Fig. 8. *Selective inversion of magnetization of free carbonates.* Experimental data (×) and fitted curve (–).

being followed by a 100-μs field stabilization delay; recovery delay 1 ms, then 2 ms, and then variable, from 2 to 30 ms by increments of 2 ms, 32 scans per spectrum, separated by 30-s relaxation delay, acquisition time, 406 ms for 4K data points. The pulse sequence uses static field gradient pulses acting z-spoils before and after the DANTE inversion pulse [24]. The DANTE pulse train is long enough (3 ms) to leave the non-selected nuclei unaffected. A longer pulse train would result in a loss of inversion efficiency by chemical exchange [25].

Data treatment: The length of the recovery delay τ is varied, and peak areas are plotted as a function of τ. The magnetization M of both species obeys *Eqn. 5.* A non-linear fitting procedure provides $k^{12}_{\mathrm{obs}} + k^{21}_{\mathrm{obs}}$. Their ratio is known from the integration of the regular ^{13}C-NMR spectrum. *Fig. 8* shows the good agreement between experimental and fitted data.

$$M = a + b \cdot \exp[-(k^{12}_{\mathrm{obs}} + k^{21}_{\mathrm{obs}})\tau] \tag{5}$$

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