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NMR and Theoretical Investigations on the Structures and Dynamics of Octahedral Bis(chelate)dichloro V^{III} Compounds Isolated by an Unusual Reduction of Non-Oxo V^{IV} Species

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Reaction of the non-oxo V^{IV} species $[V^{IV}Cl_2(L_{OO})_2]$ [L_{OO} = acetylacetonate ($acac^-$) or benzoylacetonate ($bzac^-$)] with a chelate nitrogen–donor ligand L_{NN} in acetonitrile leads to the reduction of V^{IV} to V^{III} and the formation of the mononuclear V^{III} compounds of the general formula $[V^{III}Cl_2(L_{OO})(L_{NN})]$ (L_{OO} and L_{NN} are $acac^-$ and bipy for **1**; acac- and 5,5′-me_2bipy for **2**; $acac^-$ and 4,4′-tb_2bipy for **3**; $acac^-$ and phen for **4**; $bzac^-$ and bipy for **5**; $bzac^-$ and phen for **6**). The reduction of the V^{IV} complexes was monitored by GC-MS and ^{1}H NMR spectroscopy. Both one- and two-dimensional (2D COSY and 2D EXSY) ^{1}H NMR techniques were used to assign the observed ^{1}H NMR resonances of **1**–**6** in CD_2Cl_2 or $CDCl_3$ solution. It appeared that in solution these V^{III} complexes form two isomers which are in equilibrium: *cis*-$[V^{III}Cl_2(L_{OO})(L_{NN})] \rightleftharpoons$ *trans*-$[V^{III}Cl_2(L_{OO})(L_{NN})]$. 2D EXSY cross-peaks were clearly observed between bipy- and acac-hydrogen atoms of the two geometrical isomers of **1**–**3** as well as between bipy and $acac^-$ protons of the cis isomer, indicating a dynamic process that corresponds to cis–trans isomerization and a cis–cis racemization. The thermodynamic and kinetic parameters of the equilibrium between these two isomers were calculated for compounds **1** and **2** by using variable temperature (VT) NMR data. Both cis–trans isomerization and cis–cis racemization processes probably proceed with an intramolecular twist mechanism involving a trigonal prismatic transition state. Density functional calculations (DFT) also indicated such a rearrangement mechanism.

Introduction

The design and synthesis of new metal compounds containing two labile monodentate ligands in a cis position to each other present great interest because of their antitumor and DNA binding or intercalation properties.[1] To gain insight into the mechanism of the biological activity of these molecules, it is crucial to study their structures, dynamics, and energetics. For example, the structures and dynamics of square planar *cis*-platinum antitumor compounds have been extensively studied, and significant progress has been made toward understanding the mechanism of their biological activity.[2] In contrast to the case of the square planar platinum complexes, the factors influencing the coordination modes, rearrangements, and dynamic behaviors of cis octahedral metal complexes containing heterocyclic chelating nitrogen ligands are much less understood. The latter compounds with metals such as vanadium,[3] ruthenium, or rhodium,[4] have been proved efficient to interact strongly with DNA. For example,

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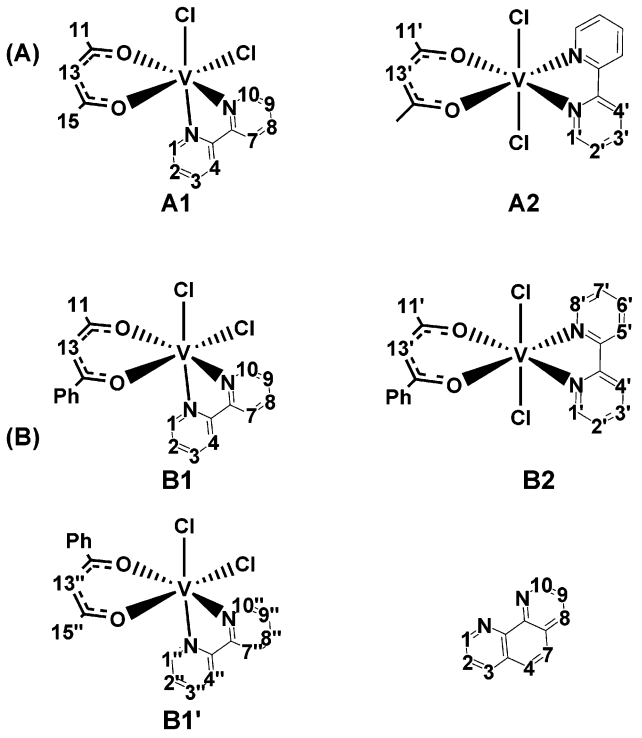
it has been recently demonstrated that V^{III} species, namely dimeric compounds of the type $[V^{III}_2O(L_{NN})_4Cl_2]^{2+}$, bind strongly to DNA and lead ultimately to its degradation.[2a] Several of these complexes are currently under investigation for their antitumor activity.[5] Vanadium compounds have remarkable antidiabetic and antitumor properties.[6] The low toxicity of the vanadium compounds in comparison with, for example, platinum compounds, is a great advantage for the vanadium species. Herein, we report the synthesis, solid-state, and ^{1}H NMR solution characterization of a series of mononuclear bis-chelate octahedral V^{III} complexes **1**−**6**, containing two additional terminal chlorine ligands. These compounds are the products of a rare reduction of the non-oxo V^{IV} precursor $[V^{IV}Cl_2(L_{OO})_2]$ in the presence of the aromatic nitrogen-donor chelate ligand L_{NN}.[7] The study of such processes might be of a great importance in order to gain insight into the mechanism of reduction of V^V (present in seawater) to V^{III} occurring during the accumulation of vanadium in ascidians.[8] More specifically, this reduction process might proceed via a V^{IV}, but more likely via a non-oxo V^{IV} intermediate species, probably formed because of a weakening of the V^{IV}═O bond in the strongly acidic environment of the ascidians' blood cells.[9] Variable temperature and 2D EXSY ^{1}H NMR spectroscopy showed that the geometrical cis- and trans-isomers of compounds **1**−**6** (Scheme 1) are in dynamic equilibrium. An intramolecular racemization for the cis-isomer of these compounds was also revealed by 2D EXSY ^{1}H NMR experiments. The possible pathways for the cis−trans isomerization and cis−cis racemization processes are discussed in the light of these ^{1}H NMR studies and density functional calculations as well.

Scheme 1. (A) Vanadium(III)-acetylacetonate Cis- and Trans-Isomers. (B) Vanadium(III)- benzoylacetylonate Cis- and Trans-Isomers



Experimental Section

Materials and Methods. All manipulations were performed under high-purity argon using standard Schlenk techniques. 2,2′-Bipyridine (bipy), 1,10-phenanthroline (phen), 5,5′-dimethyl-bipy (5,5′-me$_2$bipy), and 4,4′-di-*tert*-butyl-bipy (4,4′-tb$_2$bipy) were obtained from Aldrich and used without further purification. $[V^{IV}Cl_2(acac)_2]\cdot 0.25CH_2Cl_2$ and $[V^{IV}Cl_2(bzac)_2]$ were prepared by literature procedures.[10] Reagent grade acetonitrile was dried and distilled over calcium hydride, while diethyl ether was dried and distilled over sodium wire. C, H, N analyses were conducted by the University of Ioannina's microanalytical service; vanadium was determined gravimetrically as vanadium pentoxide or by atomic absorption, and chloride analyses were carried out by potentiometric titration.

Synthesis of $[V^{III}Cl_2(acac)(bipy)]$ (1). Solid bipy (0.247 g, 1.58 mmol) was added in one portion to a stirred suspension of $[V^{IV}Cl_2(acac)_2]\cdot 0.25CH_2Cl_2$ (0.539 g, 1.58 mmol) in CH_3CN (10 mL). Upon addition of bipy, the solution cleared and turned from dark blue to olive green. After the reaction mixture was stirred for 20 min, a yellow green precipitate was formed. Stirring was continued for 12 h, and then the precipitate was filtered off, washed with acetonitrile (2 × 5 mL) and diethyl ether (2 × 5 mL), and dried under vacuum, yielding 0.37 g of product (62% yield). Complexes **$[V^{III}Cl_2(acac)(5,5'\text{-}me_2bpy)]$ (2)**, **$[V^{III}Cl_2(acac)_2(4,4'\text{-}tb_2bipy)_2]$ (3)**, **$[V^{III}Cl_2(acac)(phen)]$ (4)**, **$[V^{III}Cl_2(bzac)(bipy)]$ (5),** and **$[V^{III}Cl_2(bzac)(phen)]$ (6)** were synthesized in a fashion similar to **1.** Elemental analyses, UV/vis, IR spectroscopic data, and conductivity measurements are given in Table S1.

Physical Measurements. IR spectra were recorded on a Perkin-Elmer Spectrum G−X FT-IR system in KBr (Mid-IR) or polyethylene (Far-IR) pellets. Electronic absorption spectra were measured

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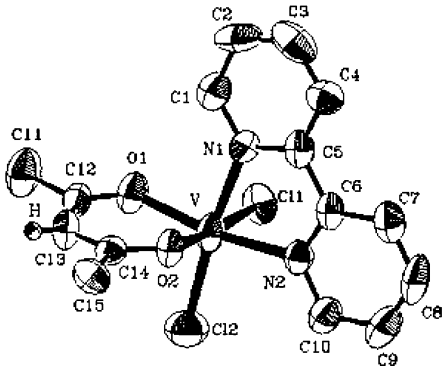

Figure 1. ORTEP diagram of **1** (from ref 7).

as solutions in septum-sealed quartz cuvettes on a Jasco V570 UV/Vis/NIR spectrophotometer. Magnetic moments were measured at room temperature by the Evans method on MK−I Sherwood Magnetic Balance. Solution conductivity data were collected in dichloromethane and methanol using a Tacussel electronique CD 6NG conductivity bridge. A temperature of 25 °C was maintained by a constant-temperature bath. The cell constant was determined to be $\kappa = 1.1025\ cm^{-1}$ by using a 0.0200 M aqueous solution of potassium chloride to calibrate the conductivity cell. ^{1}H NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300.12 MHz for ^{1}H.[12] All the calculations were performed using the Gaussian-98 package.[13−23] The experimental details and calculations for the ^{1}H NMR, variable temperature (VT), and kinetic measurements and theoretical calculations are presented in Supporting Information.

Results and Discussion

Synthesis of the Compounds. The synthesis of the mononuclear V^{III} compounds **1**−**6** results from the reduction of the non-oxo V^{IV} species $[V^{IV}Cl_2(L_{OO})_2]$, upon addition of one equivalent of bipy or phen (eq 1).

$$[V^{IV}Cl_2(L_{OO})_2] + L_{NN} \xrightarrow{CH_3CN} [V^{III}Cl_2(L_{OO})(L_{NN})] + {}'L_{OO}{}^{\bullet}{}' \quad (1)$$

L_{OO} = acac$^-$, bzac$^-$

$'L_{OO}{}^{\bullet}{}'$ = acac$^{\bullet}$, bzac$^{\bullet}$ radicals

Complex **1** was characterized by X-ray structure analysis, and it was reported in our previous communication (Figure 1).[7] In our effort to isolate a *trans*-dichloro-V^{III} species as well as to assign all the proton resonances in the ^{1}H NMR spectrum of **1**, compounds **2**−**6** were also prepared. Despite of our efforts, the crystallization of **2**−**6** for X-ray diffraction studies has been proved unsuccessful thus far. Reduction of the V^{IV} to V^{III} starts upon addition of stoichiometric quantity of the aromatic nitrogen ligand, thus indicating that the ligand induces vanadium reduction. The high yields (62−83%) in the preparation of **1**−**6** indicate that it is rather difficult to have a concurrent oxidation of the nitrogen chelate ligand. Therefore, it is reasonable to assume that the diketonate ligand or the solvent is the oxidized molecule. Diketones, however, have lower oxidation potentials than acetonitrile and they can presumably be oxidized easier from the vanadium complex.

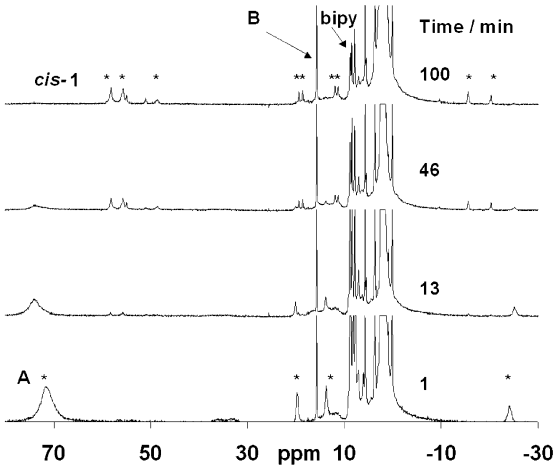

Figure 2. ^{1}H NMR spectra, obtained at various times, for the reaction of $[V^{IV}Cl_2(acac)_2]\cdot 0.25CH_2Cl_2$ (22 mM) with bipy (22 mM) in CD_3CN at 0 °C.

GC-MS (gas chromatography mass spectroscopy) and ^{1}H NMR spectroscopy were performed on the reaction mixture of **1** (vide infra) in order to identify any decomposition products. Only Hacac, bipy, and a small quantity of 3-chloro-2,4-pentanedione were detected by GC-MS. The formation of the chlorine derivative of acetylacetone is supportive of the involvement of acac$^-$ as the reducing agent of vanadium.

Investigation of the Reaction of $[V^{IV}Cl_2(acac)_2]$ with bipy by ^{1}H NMR Spectroscopy. In a dry CD_3CN solution of $[V^{IV}Cl_2(acac)_2]$ (29 mM), an equimolar quantity of bipy was added, and the reaction was followed by ^{1}H NMR spectroscopy. To slow the rate of the reaction the solution was cooled at 0 °C. Figure 2 shows the spectra at various times after the addition of bipy in the $[V^{IV}Cl_2(acac)_2]$ solution. The first spectrum shows formation of two paramagnetic vanadium species: complex **A** with peaks at 72.05 ppm (assigned to the ligated acac$^-$) and 19.68, 13.66, −24.72, and −42.35 ppm (assigned to the ligated bipy) and a complex **B** with one peak at 15.69 ppm. Additional resonances from free bipy and Hacac were also observed. The peaks' intensity of the free ligands (bipy, Hacac) and of complex **A** were progressively reduced with time. The cis-isomer of complex **1** appears ∼10 min after the addition of bipy. The *cis*-$[V^{III}Cl_2(acac)(bipy)]$ (**1**) is slightly soluble in CD_3CN, and it does precipitate out of the solution. The reaction was completed approximately 2 h after the addition of bipy as it is evidenced by the disappearance of the ^{1}H NMR peaks of free bipy and the precipitation of **1**. The ^{1}H NMR peak intensity of **B** increases much slower than the formation of **1**, and it continues to increase after the end of the reaction. Integration of the peaks of species **A** gave a ratio ∼2.3:1 between the ligated acac$^-$ and bipy, thus indicating that the chemical formula for this molecule may

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Table 1. Proton Chemical Shifts for **1**−**6** in CD_2Cl_2 or $CDCl_3$ at 293 K

	chemical shift (ppm) [T_1 (ms)]					
proton	**1**[a]	**2**[b]	**3**[b]	**4**[a]	**5**[a]	**6**[a]
1/10	−28.57/−35.00 [0.7/0.7]	−29.28/−36.41	−28.85/−35.32	−31.51/−38.89	−29.18/ −36.37	−38.07/ −46.11
9/2	18.52/17.53 [5.0/6.5]	-	19.03/18.12	19.40/18.11	18.84/17.85	16.18
3/8	−13.76/−18.65 [2.9/2.2]	−12.65/−18.53	-	−15.15/−20.53	−13.28/ −18.17	−14.11/−19.38
7/4	11.54/10.60 [3.6/5.0]	11.41/9.65	11.30/10.40	11.87/10.72	11.49/ 10.05	9.50
11/15	51.28/53.14 [2.2/2.9]	50.13/51.64	49.95/51.95	55.58/57.41	52.77	52.97
13	44.67 [1.4]	43.69	43.53	48.34	44.87	46.26
1′	−16.13 [0.7]	−17.18	−16.69	−17.78	−15.32	−19.38
2′	17.16 [6.5]	-	17.36	17.85	16.05	16.18
8′/3′	−8.59 [6.5]	−8.42	-	−9.49	−6.73/ −9.87	−6.28/ −9.74
4′	10.65 [5.0]	9.65	10.88	10.59	10.05	9.50
11′	51.02 [5.0]	51.64	49.12	54.68	55.26	55.95
13′	84.51 [0.9]	84.11	81.07	85.10	88.24	92.52
1″/10″	-	-	-	-	−29.18/ −36.37	−38.07/ −46.11
9″/2″	-	-	-	-	18.23/17.00	16.18
3″/8″	-	-	-	-	−13.34/−19.53	−14.11/−20.67
7″/4″	-	-	-	-	10.91/ 9.67	9.50
11″	-	-	-	-	55.65	58.52
13″	-	-	-	-	46.87	45.05
Ph	-	-	-	-	7.50	7.50
Me_a/Me_b	-	−6.85/ −3.51	-	-	-	-
Me_a'	-	−2.66	-	-	-	-
t-But_a/t-But_b	-	-	1.47/1.30	-	-	-
/t-But_a'	-	-	1.69	-	-	-

[a] In CD_2Cl_2 solution. [b] In $CDCl_3$ solution.

be $[V^{III}(acac)_2(bipy)]^+$. The only four aromatic ^{1}H NMR peaks observed for the eight-bipy protons of complex **A** is in accordance with the resonances expected for a symmetric compound such as $[V^{III}(acac)_2(bipy)]^+$. Additional evidence for the nature of complex **A** resulted from the ^{1}H NMR spectra of an equimolar mixture of **1** and acetylacetone in $CDCl_3$, which revealed partial conversion of **1** to complex **A**. Presumably, in solution, **1** and **A** are in equilibrium according to eq 2.

$$[V^{III}Cl_2(acac)(bipy)]\ (1) + Hacac \leftrightarrows [V^{III}(acac)_2(bipy)]^+\ (\mathbf{A}) + 2Cl^- + H^+ \quad (2)$$

Although complex **A** formed in the first minute of the reaction, the presence of free bipy in the solution indicates that only a part of bipy has reacted with the V^{VI}. ^{1}H NMR spectra did not show any equilibrium between V^{III} species and free bipy; consequently, the intensity of bipy's ^{1}H NMR peaks progressively diminished with time, indicating the progress of the V^{IV} reduction. The reduction of V^{IV} to V^{III} was completed ∼2 h after the addition of bipy in the $[V^{IV}Cl_2(acac)_2]$ solution, as it was evidenced by the disappearance of the peaks of free bipy from the ^{1}H NMR spectra. The V^{IV} starting materials did not give any ^{1}H NMR peaks in CD_3CN. ^{1}H NMR did not detect oxidized organic molecules probably because they form complexes with vanadium. Investigation of the exact mechanism of these reactions by kinetic experiments as well as full characterization of the molecules involved is under way.

Assignment of ^{1}H NMR Spectra. The solution structure of the V^{III} complexes was investigated by ^{1}H NMR spectroscopy. Scheme 1 shows the possible geometrical configurations for complexes **1**−**6**. The $acac^-$ complexes **1**−**4** may form two isomers, the cis and the trans (Scheme 1A). On the other hand, for $bzac^-$ compounds two cis-diastereoisomers and one trans-isomer are expected, since the $bzac^-$ ligand is unsymmetrical (Scheme 1B). The cis-diastereoisomers do not possess any symmetry elements. The cis-isomers of compounds **1**−**4** have eight nonequivalent bipy or phen aromatic protons as well as two nonequivalent sets of $acac^-$ methyl protons and an $acac^-$ ring proton. On the other hand, in the trans-isomers (C_{2v} symmetry) are expected four nonequivalent bipy or phen protons as well as a single methyl and a single ring $acac^-$ proton environment. In the cis/trans-isomers of **5** and **6** there are eight nonequivalent bipy or phen aromatic protons but only one set of $bzac^-$ protons for each compound.

The ^{1}H NMR spectra of **1**−**6** in CD_2Cl_2 or $CDCl_3$ solution, revealed isotropically shifted signals in the (+85)−(−40) ppm chemical shift range at 20 °C (slow exchange conditions), assigned to both cis/trans-isomers. Chemical shifts and assignments of the compounds in CD_2Cl_2 and $CDCl_3$ solutions together with the calculated T_1 values for **1** are listed in Table 1. The numbering of the ligands is shown in Scheme 1.

Excluding the signals from the CD_2Cl_2 and its impurities as well as some peaks resulting from partial decomposition of **1** in solution, 17 isotropically shifted signals are observed. Eleven of the peaks, which is exactly the number expected for the cis-isomer, were predominant and they approximately consist 85% of all peaks' intensity. The remaining six resonances were assigned to the trans-isomer. The assignment of the bipy resonances for both isomers was facilitated by Me and t-Bu substitution at the A1(2), A1(9), A2(2′) (complex **2**) and A1(3), A1(8), A2(3′) (complex **3**); the other resonance positions did not differ much between **1**, **2**, and **3**. Furthermore, the ^{1}H NMR spectrum of the $bzac^-$ derivative (complex **5**) was used to distinguish the bipy protons of *cis*-**1.** The A1(1), A1(10), A2(1′) bipy hydrogen atoms are the closest to the metal centers and consequently gave the

most paramagnetically broadened resonances at −28.6, −35.0, and −16.1 ppm, respectively. The remaining resonances at 18.52, 17.53, and 17.16 ppm are then assigned by elimination to the A1(7), A1(4), and A2(4′) hydrogen atoms. Additional proof for the correct assignments was acquired from the 2D COSY spectrum, which gave cross-peaks between the neighboring bipy hydrogen atoms. The remaining four peaks in the range 60−90 ppm were assigned to acac$^-$ protons. The chemical shifts of these resonances are in agreement with the shifts observed for [V^{III}(acac)$_3$],[24] with the exception of the methylene protons of the trans-isomer which have shifted further downfield at 84.51 ppm.

Orbitally nondegenerate systems such as the nonsymmetric complexes **1**−**6** reported here are expected to have no significant pseudo-contact shifts. Consequently, the shifts provide direct information regarding the mechanism of spin delocalization.[25] The bipy resonances display the alternating shift pattern characteristic of contact shifts resulting from spin delocalization onto the bipy ligand via a π delocalization pathway.[26] Thus, the A1(1), A1(10), A2(1′), A1(3), A1(8), A2(3′) hydrogen atoms are paramagnetically shifted upfield, while the A1(2), A1(9), A2(2′), A1(4), A1(7), A2(4′) are shifted downfield. In addition, the π spin delocalization mechanism was supported by the change in sign of the isotropic shifts of the A1(2), A1(9), A2(2′) methyl groups (complex **2)** compared to the shifts of hydrogen atoms at these positions (complex **1)** (Table 1). The isotropically shifted resonance of the methylene acac$^-$ proton also results from delocalization of the unpaired spin density through π bonds. Apparently the larger downfield shift observed for the methylene acac$^-$ proton of the trans-isomers, compared with the cis-isomers, shows a more effective delocalization of the unpaired spin onto the acac$^-$ ligand for the former isomers. This is probably due to a better overlap of the d_π V^{III} orbitals with the π orbitals of acac$^-$ for the trans-species.

Table 2. Thermodynamic and Kinetic Parameters for Cis−Trans and Cis−Cis Rearrangements for **1** and **2** in $CDCl_3$ and in CD_2Cl_2 (data in parentheses)

	1		**2**	
	cis−trans	cis−cis	cis−trans	cis−cis
[trans]/[cis] (293 K) [1]	0.78 (0.15)		0.72	
ΔH (kcal/mol)	1.8 ± 0.1 (2.6 ± 0.4)		0.72 ± 0.13	
ΔS (cal/mol/deg)	2.8 ± 0.4 (5.4 ± 1.6)		1.8 ± 0.4	
ΔG (298 K) (kcal/mol)	0.25 ± 0.02 (1.0 ± 0.9)		0.18 ± 0.26	
$\Delta H^‡$ (kcal/mol)	16.7 ± 0.9	13.4 ± 0.7	17.9 ± 1.2	16.7 ± 1.5
$\Delta S^‡$ (cal/mol/deg)	3.7 ± 2.8	−5.6 ± 2.7	5.8 ± 3.4	3.1 ± 4.7
$\Delta G^‡$ (298 K) (kcal/mol)	15.6 ± 1.7	15.0 ± 1.6	16.1 ± 2.3	15.7 ± 2.9
E_a (kcal/mol)[2]	17.3 ± 0.9	14.0 ± 0.9		

[1] [trans]/[cis] ratio for complexes **3**−**6** in CD_2Cl_2 at 293 K is ∼0.15. [2] E_a was calculated from Arrhenius plot [ln(k) vs 1/T].

Stability of Cis−Trans Isomers in Solution. The exact concentrations of the cis- and trans-isomers can conveniently be monitored by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of complexes **1**−**6** did not show any significant variations in the magnitude of the ratio [trans]/[cis], but they proved to be strongly dependent on the solvent used. Thus, upon decreasing the polarity of the solvent, an increasing [trans]/[cis] ratio is observed (Table 2). This was consistent with the stabilization of the more polar cis-isomers, expected in solvents of higher polarity, due to solvation effects.

Within the slow exchange temperature range 233−298 K in $CDCl_3$ and 228−298 K in CD_2Cl_2, the changes for the [trans]/[cis] ratios were determined for complexes **1** and **2**. The ^{1}H NMR spectra in these temperature ranges showed that higher temperatures favored the trans-isomer. The thermodynamic parameters for this equilibrium were determined from the Van't Hoff plot, and the data are shown in Table 2. These values showed that the trans-isomer is slightly favored entropically (positive ΔS), but it is slightly disfavored enthalpically (positive ΔH). The solvation of the isomers is probably the major reason for the observed thermodynamic values which is further supported by the increasing ΔS and ΔH values in more polar solvents (Table 2), as expected assuming that cis-isomers are better solvated in more polar solvents than the trans ones.

Kinetics of Cis−Cis and Cis−Trans Rearrangements. The kinetics of complexes **1**−**3** were examined using variable temperature and 2D EXSY ^{1}H NMR spectroscopy. The low solubility of compounds **4**−**6** did not allow us to perform such experiments for these molecules. The CD_2Cl_2 and $CDCl_3$ solutions of V^{III} complexes **1**−**6** gave well-resolved resonances at room temperature suggesting that the exchange between the cis- and trans-isomers and the racemization of the nonsymmetric cis-isomers are slow processes with respect to the NMR time scale. However, upon increasing the temperature up to 65 °C (upper limit for $CDCl_3$) for the $CDCl_3$ solutions of complexes **1** and **2**, the three signals from acetylacetonate methyl protons (two from the cis- and one from the trans-isomer) as well as the bipyridine protons A1-(2), A1(9), A2(2′) and A1(4), A1(7), A2(4′) became broader and finally coalesced to give three single peaks. Similarly, the resonances of A1(1), A1(10), A2(1′) and A1(3), A1(8), A2(3′) as well as the methylene acetyloacetonate protons

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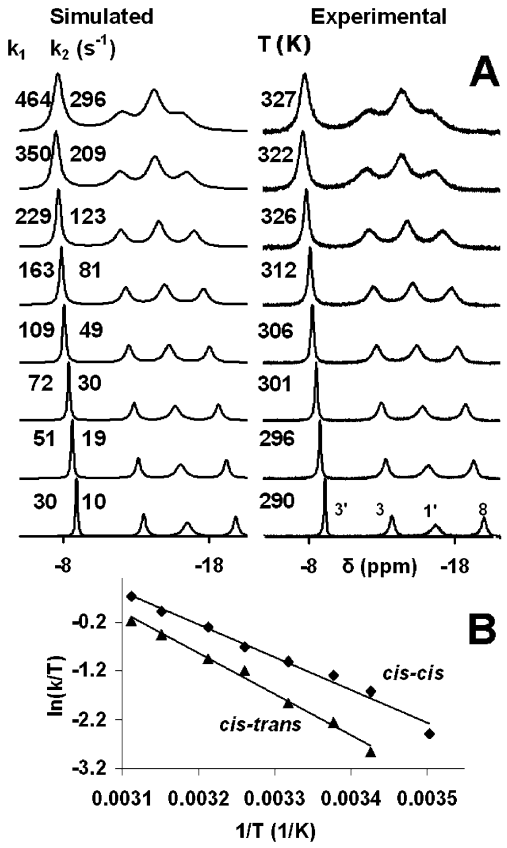

Figure 3. (A) Variable temperature ^{1}H NMR spectra of 3,8,3′,8′ protons of **1** in $CDCl_3$ solution. The experimental and simulated spectra are on the right- and left-hand side, respectively. The rate constants for the cis−trans isomerization (k_2) and the cis−cis racemization (k_1) are also shown. (B) Eyring plots for cis−cis and cis−trans rearrangements of complex **1**.

[A1(13), A2(13′)] became broader at higher temperatures, but never coalesced due to the large chemical shift differences (Figure 3). Line-shape analysis of the experimental spectra afforded the respective calculated spectra and the rate constants for cis−cis racemization and cis−trans isomerization (see Figure 3). The rate constants were fitted as a function of $1/T$ according to the Eyring equation to obtain the activation parameters for complexes **1** and **2** (Table 2 and Figure 3).

Cis−trans isomerization and a cis−cis racemization exchange for the peaks of the bipy aromatic hydrogen atoms and the two acac$^-$ methyl resonances of complexes **1**−**3** were revealed by cross signals in the ^{1}H 2D EXSY experiments using mixing times 3 ms (Figure 4).

Investigations on the Possible Mechanisms for the Cis−Cis Racemization and Cis−Trans Isomerization Processes. Isomerization or racemization of bis(chelate) octahedral $[M(LL)_2X_2]$ complexes may proceed through an intermolecular or intramolecular mechanism.[27] The intermolecular mechanisms may involve dissociation of a monodentate ligand to give a five-coordinate intermediate or complete dissociation of a chelate ligand to yield a four-coordinate intermediate. The two possible intramolecular mechanisms are (i) momentary rupture of one metal−chelate ligand bond to give a trigonal bipyramidal or (ii) a square-pyramidal transition state or twist motions of the ligands to give an idealized trigonal-prismatic transition state.[27] To investigate first if intermolecular mechanisms are involved in this cis−trans and cis−cis exchange, the 1D ^{1}H and the 2D EXSY NMR spectra of $CDCl_3$ solutions of **1** containing equimolar quantities of bipy, Hacac, or tetrabutylammonium chloride were acquired. The line shape of the resonances and the exchange rates were not altered by adding these molecules to the solutions of the complexes, and the 2D EXSY spectra did not show any cross-peaks between free and coordinated bipy or acac$^-$. These observations indicated that the intermolecular exchange between the free and coordinated ligands, if existing, is much slower compared to the observed cis−trans and cis−cis exchange. This is in

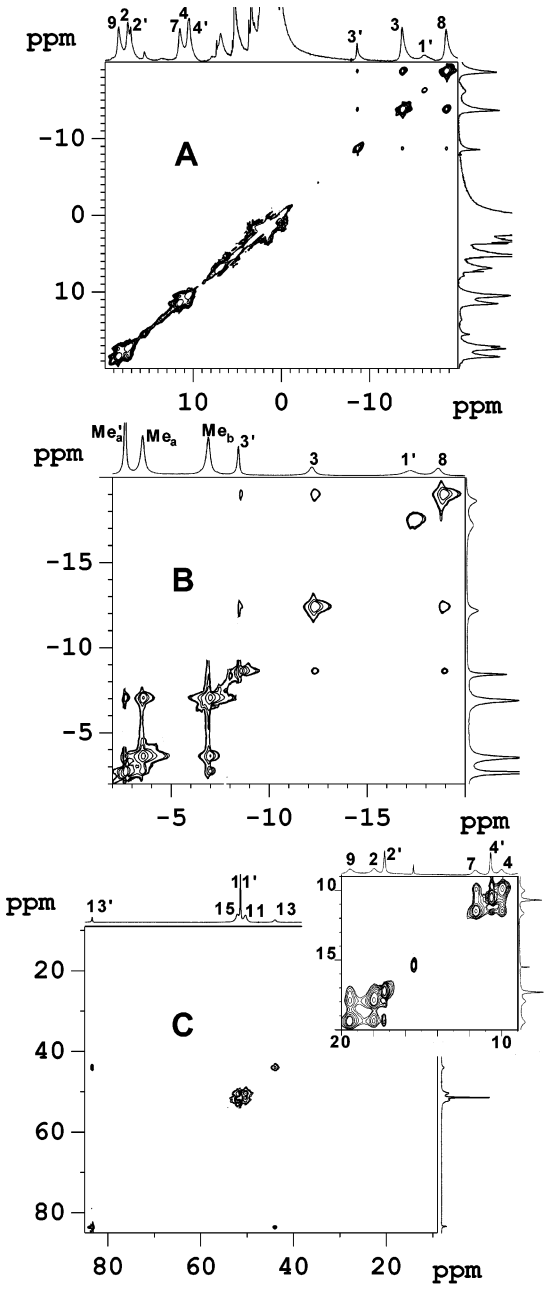

Figure 4. 2D ^{1}H EXSY spectrum of **1** (A) in CD_2Cl_2, and **2** (B) and **3** (C) in $CDCl_3$, at 293 K. Conditions are given in the text.

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Table 3. Kinetic Parameters for the Intramolecular Rearrangements of Bis-Chelate Molecules[a]

compound[a]	solvent	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/K·mol	$\Delta G^{\ddagger 298}$, kcal/mol	mechanism	ref
$[V^{III}(L_{NN})(L_{OO})Cl_2]$ L_{NN} = bipy, phen L_{OO} = acac, bzac	$CDCl_3$	15 to17	−5 to 6	15 to16	twist	this work
$[Ti^{IV}(acac)_2(OR)_2]$	$CDCl_3$	12 to 16	−6 to −12	15 to 18	twist	30b
$[Ti^{IV}(dmp)_2(OR)_2]$	$CDCl_3$	12 to 17	−7 to −12	16 to 21	twist	30b
$[Ti^{IV}(acac)_2X_2]$ X = Cl, Br	CD_2Cl_2		−2 to −10		twist	31c
$[Ti^{IV}(Me_2dtp)_2X_2]$ X = Cl, OR	CD_2Cl_2	10 to 14	−12 to 6	11 to 13	bond rupture	31b
$[Co^{III}(dtc)_2(PHPh_2)_2]^+$	CD_3CN	28.7	12	25	twist	32

[a] dtc = dithiocarbamates, dpm = 2,2,6,6-tetramethyl-3,5-hexanedione, dtp = dithiophosphate.

line with the small $acac^-$ exchange rate (6×10^{-4} s^{-1} at 25 °C in $CHCl_3$) observed for the complex $[V^{III}(acac)_3]$,[28] which is much lower than the rearrangement rates (30 and 10 s^{-1} for cis−cis and cis−trans, respectively, at 25 °C) for complex **1**. Although the exchange rate of bipy has not been measured for other V^{III} complexes, it is rather unlikely for this chelate ligand to exchange much faster than $acac^-$. In addition, the exchange of weak monodentate ligands such as DMSO in V^{III} compounds is relatively slow (13.1 ± 1.5 s^{-1} at 25 °C in DMSO),[29] strengthening our belief that these rearrangements proceed through an intramolecular mechanism. Furthermore, the intermolecular exchange reactions reported in the literature for the V^{III} compounds with chelate or monodentate ligands have negative activation entropies (∼−15 cal K^{-1} mol^{-1}),[28] in contrast to the small positive or negative activation entropy (Table 2) observed for **1** and **2,** respectively, supporting an intramolecular mechanism.[30]

A literature survey for the rearrangement reactions of bis(chelate) metal compounds revealed activation entropy for bond rupture and twist mechanisms ranging between −20 to +20 cal K^{-1} mol^{-1}.[31] Therefore, it appears tenuous to make claims about the intramolecular mechanisms on the basis of activation entropies only. The activation enthalpy observed for the intermolecular exchange in the $[V^{III}(acac)_3]$-Hacac system (18.0 ± 1.3 kcal mol^{-1}), in which an associative acetylacetonate bond rupture mechanism has been proposed, is slightly larger than the activation enthalpies of the rearrangement reactions of **1** and **2** (Table 2). The high activation enthalpy of this reaction has been considered responsible for the inertness of $[V^{III}(acac)_3]$ and is in contrast to the greater lability (∼10 000-fold) in the racemization and isomerization of **1** and **2**, indicating that the V−O bond rupture mechanism for these two processes is rather improbable.

Certain trends of the activation parameters reported in the literature for the rearrangement reactions of other bis(chelate) metal compounds and those of **1** and **2** may give some indication for the type of mechanism (Table 3). Ti^{IV} bis(chelate) molecules that follow a twist mechanism for the intramolecular cis−cis rearrangements exhibit larger activation enthalpies than $[Ti^{IV}(Me_2dtp)_2X_2]$, which rearranges through a bond rupture mechanism (Table 3). In addition to the titanium compounds, the rest of the complexes presented in Table 3, exhibiting twist cis−trans and/or cis−cis rearrangments, show large activation enthalpies and near zero activation entropies. The most interesting feature in this table that supports a twist over a bond rupture mechanism for **1** and **2** may be that all the bis-chelate diketonate complexes that rearrange by a twist mechanism including **1** and **2** have activation free energies in a very narrow range between 15 and 18 kcal mol^{-1}. This is expected, considering that twist mechanisms are independent of the metal−ligand bond strength and are dependent on the bulkiness of the ligand (bulkier monodentate ligands decrease the rate of a twist mechanism).[30a]

Among all the pathways of Bailar twists that can be performed on **1**, only one transformation, namely, the cis-bis(chelate) isomer to trans- or to cis-enantiomer, can result in two products, whereas three pathways transform only to the cis-enantiomer.[33] These twists proceed about the four axes 1, 2, 3 and 4 represented in Scheme 2A. The stereochemical result of performing the corresponding twists 1, 2, 3, and 4 is represented in Scheme 2B. Apparently cis−trans rearrangement can only occur through rotation around axis 1, whereas all pathways are probable for cis−cis racemization. These paths are not equivalent, and the differentiation of energetics will depend on many factors, perhaps more importantly on chelate ring flexibility and steric factors. It is worth noting here that the cis−cis rearrangements are faster than cis−trans rearrangement for **1** and **2**, thus indicating that the intermediates or transition states for cis−cis will be more stable than cis−trans conversions. There are two possible scenarios for these reactions: (a) both processes follow the same path with twist around axis 1. The faster rates for cis−cis compared to cis−trans rearrangements could be attributed to lower stability of TS_{a1} and TS_{a3} compared to TS_{a2} intermediate (Scheme 2), and (b) cis−trans follow path 1 whereas cis−cis follow paths 2, 3, and/or 4 with TS_b, TS_c, and/or TS_d to be more stable than TS_{a2} (Scheme 2).

Complexes of the type $[M(AA)X_2]$ or $[M(AB)X_2]$, where AA/AB = diketonate ligands, X = halogen, alkyl, phenyl, or alkoxide group, for M = Sn^{IV} [33a] did not favor twist around

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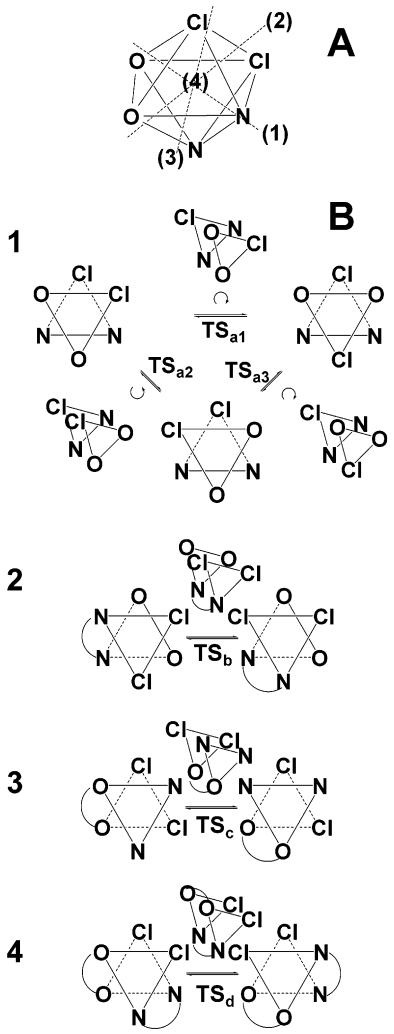
Scheme 2. (A) The Four Axes 1, 2, 3, and 4, about Which Bailar Twists Can Be Performed. (B) the Mechanisms of Bailar Twists about Axes 1−4



axis 1, whereas for the related Ti^{IV},[30b] complexes twisting around 1 and/or 4 are favored only by steric congestion on X. These data show that scenario b will be the most probable for the cis−cis racemization and cis−trans isomerization reactions for **1** and **2**.

Theoretical Calculations on Compound 1. Full geometry optimizations starting from appropriate geometries were carried out without symmetry constraints and gave two minima, namely *cis*-[V^{III}Cl$_2$(acac)(bipy)] and *trans*-[V^{III}Cl$_2$-(acac)(bpy)]. Both isomers are minima in the potential surface of the molecule, as the calculation of the Hessian gave no imaginary frequencies. The trans-isomer, which has essentially C_{2v} symmetry, is found to be the global minimum, whereas the cis-isomer has been found to be only 2.8 kcal/mol higher in energy, a fact that contradicts the experimental observations. As the dipole moment of the cis-isomer at the gas phase (12.2 D) was predicted to be considerably larger than that of the trans-isomer (6.2 D), one expects that a polar solvent would significantly stabilize the cis-isomer.

According to preliminary single point calculations on the optimized gas-phase structures in the presence of solvent (acetone), the stabilization energy due to the solvent was calculated equal to 16 and 10 kcal/mol for the cis and trans structures, respectively. Thus, the two mimima were fully reoptimized in the presence of the solvent, starting from the geometries calculated in the gas phase and the energy ordering of the two isomers has been inversed with the cis isomer being more stable by 2.1 kcal/mol in agreement with the experiment. There are no major differences between the gas-phase structures and those calculated in the presence of the solvent (Figure S4, Table S2).

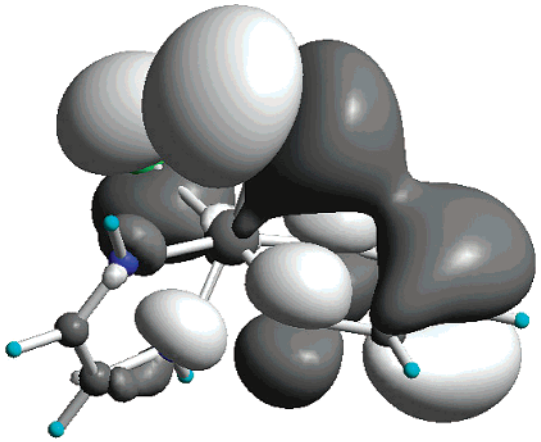


Figure 5. Shape of the occupied bonding molecular orbital resulting from the p_{Cl}/π^*_{acac} interaction calculated at the DFT level. Only atoms whose atomic orbitals participate in the molecular orbital are shown.

In both the experimental and calculated structure the acac$^-$ bends toward chlorine while keeping its planarity. Thus, in the experimental structure the (O−V−O) plane makes an angle of 18.7° with the (O−C−C−C−O) mean plane (Figure 1), whereas this angle is 21.3° in the calculated structure. Attempts to optimize a cis structure starting with a nonbent acac$^-$ ligand collapses to the same distorted minimum. No such bending exists in the calculated trans-isomer, a fact that is not imposed by symmetry, as no symmetry constraints have been applied during optimization. Having excluded any steric hindrance responsible for this bending, we carefully examined the calculated molecular orbitals. Indeed, there is an orbital interaction that stabilizes the system and apparently leads to such a distortion. A filled p-orbital of Cl(2) interacts with a π^* orbital of the acac$^-$ ligand, resulting in stabilization of the system. The shape of the occupied bonding molecular orbital resulting from this interaction, calculated at the DFT level, is shown in Figure 5.

Because of the shallowness of the potential energy surface in the region of the two minima we undertook a computational study of a possible cis − trans interconversion, trying to locate a transition state connecting the two minima in the presence of the solvent. Because of the large size of the complex and with the aim to speed up the calculations this study was undertaken using a model in which, the bipy ligand was replaced by the model ligand [HN═CH−CH═NH], which has the same donor atoms and compares well with the conjugated system of bipy.[34] The cis and trans structures of the model complex were fully optimized. The cis-isomer is 2.3 kcal/mol more stable than the trans one, a value very close to that found for the actual complex. Also, the

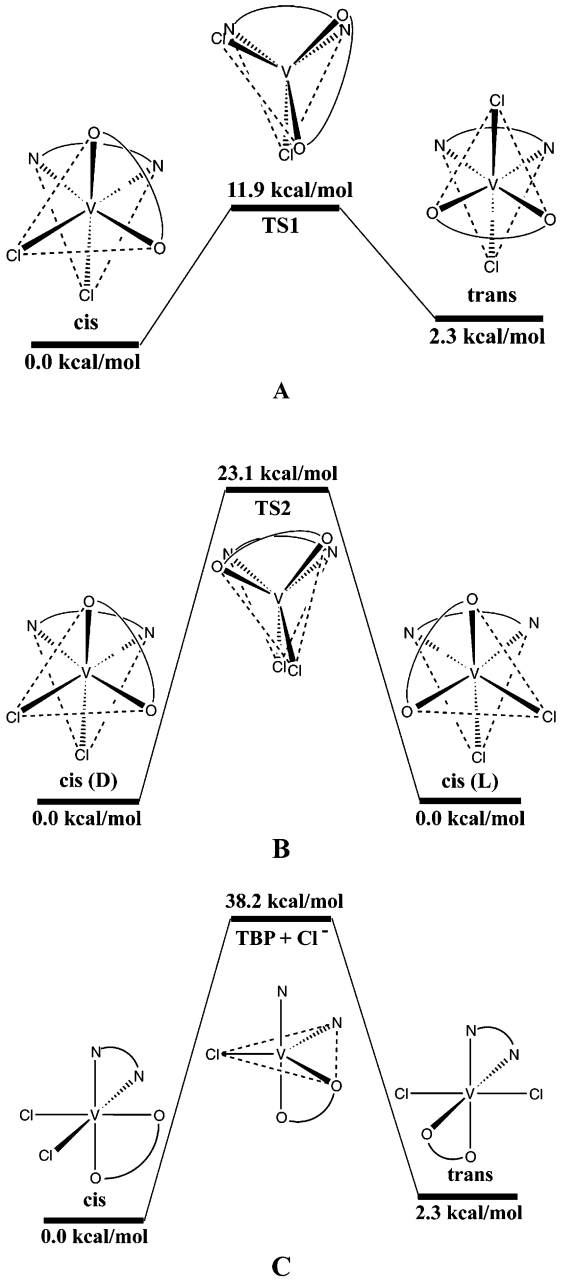


Figure 6. Possible means of nondissociative cis−trans isomerization (A), racemization (B), and dissociative cis−trans isomerization (C) for the model complex of **1** in the presence of solvent.

optimized geometries of the model complex are very close to those of the actual complex (Figure S5).

The relative energies of the various species found in the course of exploring the potential energy surface of the model complex and the possible means of isomerization or racemization are shown in Figure 6. The two transition states found, $\mathbf{TS_{a1}}$ and $\mathbf{TS_{a2}}$, related to pathways without bond rupture are shown in Scheme 2 (pathway 1). They have trigonal prismatic configurations resulting from a trigonal shift of the molecule. The imaginary frequencies have been calculated equal to 68 and 75 cm^{-1} for $\mathbf{TS_{a1}}$ and $\mathbf{TS_{a2}}$, respectively. Calculation of the IRC in each case showed that $\mathbf{TS_{a1}}$ is located at the saddle point in the pathway connecting the cis and trans structures (Figure 6A), whereas $\mathbf{TS_{a2}}$ at a saddle point related with the interconversion of the two enantiomeric forms of the cis-isomer (Figure 6B). The activation barriers calculated for the cis−trans isomerization and cis−cis racemization are 11.9 and 23.1 kcal/mol, respectively. Activation energies of this magnitude could result in rates of rearrangements in the range of 10^2-10^5 s^{-1} at temperatures between +150 °C and −150 °C.

Finally, the following dissociative pathway with a 5-coordinate intermediate adopting a square pyramidal (SP) or trigonal bipyramidal (TBP) structure has been examined:

$$\textit{cis}\text{-}[V^{III}Cl_2(acac)(bipy)] \leftrightarrows [V^{III}Cl(acac)(bipy)]^+ + Cl^- \leftrightarrows \textit{trans}\text{-}[V^{III}Cl_2(acac)(bipy)]$$

The trigonal bipyramidal geometry, **TBP**, is the only real minimum structure found in the potential energy surface of the five-coordinate $[V^{III}Cl(acac)(bipy)]^+$. Its optimized geometry is shown in Figure S6. The dissociation energy of *cis*-$[V^{III}Cl_2(acac)(bipy)]$ is 38.2 kcal/mol. Although no transition state related to this dissociation was found, the activation energy for the dissociative interconversion (Figure 6C), if any, would be greater than 38.2 kcal/mol. It is therefore concluded that this process does not occur under normal conditions because of the large barrier.

In general the theoretical calculations are in good agreement with the NMR data. Using the NMR and the theoretical studies we are proposing an intramolecular twist mechanism for the isomerization and racemication reactions of the V^{III} complexes. The theoretically calculated activation barriers for cis−cis and cis−trans rearrangements assuming path 1 for the twist of V^{III} complexes are very close to the experimental values from the NMR. In contrast to the NMR data, cis−cis rearrangement was found to be slower than cis−trans twist, thus indicating that cis−cis twist prefers axis 2 and/or 3 (scenario b). Path 4 probably will have higher activation barrier similar to path 1 for the cis−cis rearrangement due to the Cl−Cl steric interactions in the transition state (Scheme 2).

Conclusions

A series of bis(chelate)V^{III} mononuclear compounds **1**−**6** containing two terminal chlorine ligands were isolated by treating a non-oxo V^{IV} precursor with bipy or phen in acetonitrile. The diketonate ligand of the V^{IV} precursor is the more probable reducing agent in the preparations of **1**−**6**, as evidenced by the detection of a chloro-diketonate derivative by GC-MS and taking into account the high yields in these preparations. These syntheses revealed that the reduction of non-oxo V^{IV} species could easily proceed in the presence of ligands that are able to stabilize V^{III}. Thus, it cannot be excluded that the $V^{IV}O^{2+} \rightarrow V^{III}$ reduction in ascidians might be facilitated by the formation of a non-oxo V^{IV} intermediate species in the strongly acidic environment

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of the blood cells of ascidians. We are currently testing the ability of biologically relevant nitrogen-donor ligands, such as imidazole- or pyrimidine-containing organic groups, to facilitate the reduction of non-oxo V^{IV} species.

The two geometrical isomers of the acetylacetonate V^{III} compounds **1**-**4** and the three isomers of the respective benzoylacetonate V^{III} species **5** and **6** are resolved in their ^{1}H NMR spectrum in $CDCl_3$ or CD_2Cl_2 solution. Although **1** may form two geometrical isomers, only its cis-isomer was crystallized. On the basis of the thermodynamic parameters calculated by VT ^{1}H NMR spectroscopy and on DFT calculations, this is attributed to the greater stability of the cis-isomer due to the better solvation in the polar solvents (e.g., acetone). The VT and the 2D EXSY ^{1}H NMR studies demonstrated that compounds **1**−**6** are involved in a cis−trans isomerization and a cis−cis racemization processes. The calculated activation parameters for these processes led us to propose an intramolecular trigonal twist mechanism for both rearrangements. The theoretical calculations also agreed with the proposed by NMR trigonal twist mechanism. These data taken collectively suggest that ^{1}H NMR might be a viable tool for studying the dynamics and structures of mononuclear V^{III} species in solution.

Supporting Information Available: Figures S1−S6; a table of bond distances and angles for the cis- and trans-isomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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