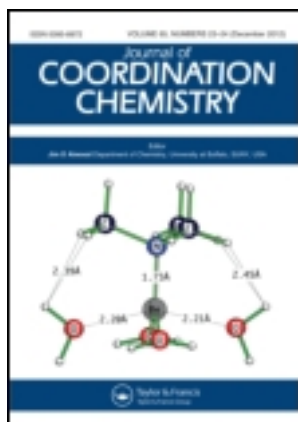


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### Water exchange on beryllium complexes: part VIII - influence of neutral electron pair donors

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## Water exchange on beryllium complexes: part VIII – influence of neutral electron pair donors<sup>1</sup>

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In this article, water exchange reactions on  $[\text{Be}(\text{L})(\text{H}_2\text{O})_3]^{2+}$  ( $\text{L} = \text{NH}_{3-x}(\text{CH}_3)_x$ ,  $\text{PH}_{3-x}(\text{CH}_3)_x$ ,  $\text{AsH}_{3-x}(\text{CH}_3)_x$ ,  $\text{OH}_{2-x}(\text{CH}_3)_x$ ,  $\text{SH}_{2-x}(\text{CH}_3)_x$ ,  $\text{SeH}_{2-x}(\text{CH}_3)_x$ , pyridine, 4-fluoropyridine, 4-bromopyridine, 4-chloropyridine, 4-hydroxypyridine, 4-thiopyridine, 4-selenidopyridine, 4-nitriropyridine, 1,4-diazine, 1,3,5-triazine, HCN, acetonitrile, and benzonitrile) are examined, utilizing the B3LYP//6-311 + G\*\* density functional for geometry optimizations, and B3LYP//6-311 + G\*\* both with and without the CPCM solvent model as well as MP2(full)//6-311 + G\*\* for subsequent single-point energy calculations. In all examined cases, the results prove that these complexes show associative interchange mechanisms for water exchange. With the exception of the  $\text{NH}_x(\text{CH}_3)_{3-x}$  series of ligands, activation energy barriers vary little, making these ligands mostly spectator ligands. Geometrical parameters vary mainly with the ligand size.

**Keywords:** Beryllium; Solvent exchange; Quantum-chemical calculations; Ligand effects

### 1. Introduction

Beryllium is found in the Earth's crust at average concentrations of 2.8–5.0 mg kg<sup>-1</sup>. While not incorporated in any known biological processes, beryllium is nonetheless a vital element. Without it, carbon synthesis from helium nuclei inside stars is impossible and would preclude the synthesis of any heavier elements, and therefore of any life. Its unique physicochemical properties, such as a very high strength to mass ratio, stiffness, electrical and thermal conductivity, corrosion resistance, and nuclear properties, make it useful or sometimes even essential in important technological applications [1]. However, utilization of beryllium and beryllium compounds is greatly hindered by negative health effects, the extent of which is still under discussion. In particular, exposure to beryllium and its compounds causes chronic beryllium disease in

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<sup>1</sup>For part VII, see: M. Walther, R. Puchta. *RSC Advances*, **2**, 5815 (2012).

susceptible individuals, a granulomatous disorder of the lungs, which is devastating, incurable, and potentially fatal [2]. Furthermore, beryllium compounds can also cause contact dermatitis, and beryllium and its compounds are carcinogenic for both animals and humans [3]. At present, no widely accepted antidote for beryllium poisoning is available [4].

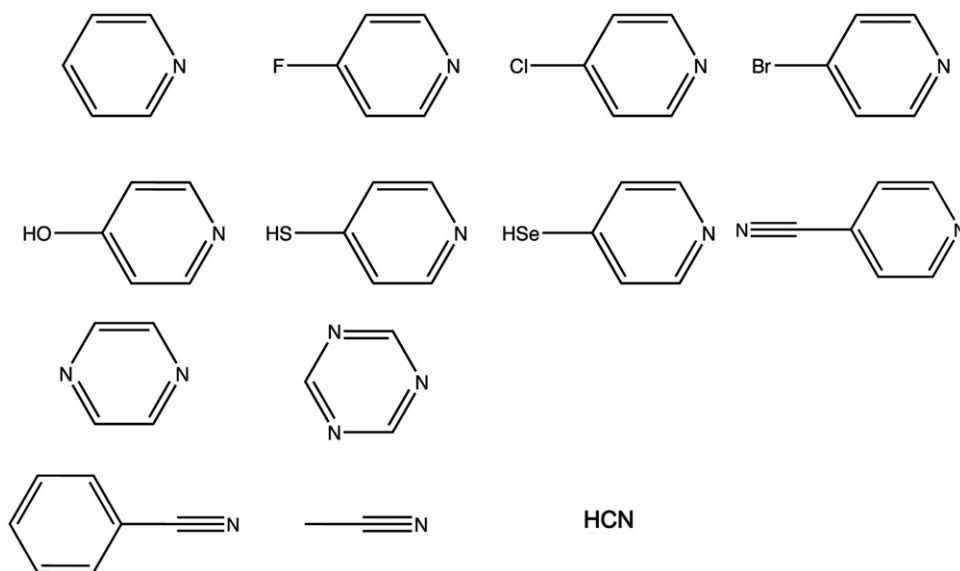
The combination of beryllium's utility, toxicity, and widespread use makes it essential to further understand beryllium chemistry, in particular, coordination chemistry in aqueous solution, since a large part of the industrial chemistry of beryllium and all its toxicity are based on equilibria in aqueous solution. The coordination chemistry of beryllium in aqueous solution may serve as the basis for future development in understanding the factors, which lead to diseases and factors involved in the design of potential cures and therapeutics [5–8].

Exchange of a water molecule between the first coordination sphere and bulk water is fundamental to understanding reactivity of metal ions in solution. Although, it is a totally symmetric reaction that involves no net chemical change, it is a dynamic process that controls the rate and mechanisms of complex formation and ligand substitution reactions. The water-exchange reaction is elucidated in terms of the classification of Gray and Langford [9], which describes two limiting mechanisms, associative (A) and dissociative (D), and three intermediate categories, the associative interchange ( $I_a$ ), interchange ( $I$ ), and dissociative interchange ( $I_d$ ). In the interchange mechanisms, the importance of the contributions coming from bond breaking or bond making is used as a theoretical classification criterion. After the publication of Eyring's reaction rate theory, activation volume ( $\Delta V^\ddagger$ ) [10] became a recognized experimental criterion for classification of reaction mechanisms [11]. The experimental and theoretical aspects of water-exchange reactions within this concept have been extensively reviewed [12–16].

The beryllium dication with an ionic radius of only 35 pm has rather interesting properties both in organo-metal chemistry [17] and classical coordination chemistry [18]. It is typically four-coordinate in aqueous solution, with a tetrahedral structure as shown by calculations and experiments [19–21]. Studies on the water-exchange mechanism of  $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$  were conducted by Merbach *et al.* [22] using high-pressure NMR. The experimentally determined volume of activation of  $-13.6 \text{ cm}^3 \text{ mol}^{-1}$  for water exchange around  $\text{Be}^{2+}$  implies that water exchange on  $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$  proceeds via an associative mechanism [22].

Motivated by the experimental kinetic measurements, we conducted extensive studies of the solvent exchange reaction on solvated  $\text{Be}^{2+}$  using quantum-mechanical methods. First, we focused on small solvent molecules with O- and N-donors of different hybridization ( $\text{H}_2\text{O}$ ,  $\text{H}_2\text{CO}$ ,  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{HCN}$ ,  $\text{N}_2$ , etc.). On the basis of the calculated Be–solvent distances in the transition states, an associative interchange mechanism was suggested for all studied exchange reactions [23]. Similar mechanistic results for the exchange of water and ammonia on beryllium dications were found for coordination with both a chelating crown ether (12-crown-4) [24] and an imidazole-based chelating ligand [25]. An associative interchange mechanism was further confirmed in our recent quantum chemical investigations on the water-exchange mechanism of four-coordinate complexes of the type  $[\text{Be}(\text{H}_2\text{O})_3(\text{X})]^+$  for  $\text{X} = \text{H}^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{OH}^-$ ,  $\text{CN}^-$ ,  $\text{CNCN}^-$ ,  $\text{NCNCN}^-$ , and  $\text{NCNCN}^-$  [26].

To learn about possible influences of L in  $[\text{Be}(\text{L})(\text{H}_2\text{O})_3]^{2+}$ , we extend our quantum chemical investigations on water-exchange mechanism of four-coordinate complexes of the type  $[\text{Be}(\text{L})(\text{H}_2\text{O})_3]^{2+}$ , where L represents various neutral ligands. First, we



Scheme 1. Examined ensemble of ligands.

investigated complexes with the hydrogen compounds of N, P, As, O, S, and Se, and their methyl-substituted analogs, all  $sp^3$ -hybridized:  $NH_{3-x}(CH_3)_x$ ,  $PH_{3-x}(CH_3)_x$ ,  $AsH_{3-x}(CH_3)_x$ ,  $OH_{2-x}(CH_3)_x$ ,  $SH_{2-x}(CH_3)_x$ , and  $SeH_{2-x}(CH_3)_x$ . In addition, we studied ligands with N- $sp^2$  hybridization.

We also studied ligands with N- $sp$  hybridization (scheme 1).

Keeping in mind the pioneering work of Evans, Rustad, and Casey on the problem of potential parallel reaction pathways depending on the solvation sphere around the metal ion center [27], we chose both the smallest possible ensemble  $[Be(L)(H_2O)_3]^{2+}$  together with  $H_2O$  and applied the highest possible symmetry, too. With the limitations of this model's framework we prevent structures biased by different number of hydrogen bonds, different hydrogen bonding patterns, or different conformations of the water molecules bound by hydrogen bonds, and additionally ensured a symmetrical reaction pathway.

## 2. Results and discussion

In all the cases, water-exchange reactions followed the pathway outlined in figure 1. In a first step, a fourth water molecule entered into the second coordination sphere. In a subsequent step, this molecule enters the first coordination sphere and exchanges with another water, passing the transition state, but not forming a stable five-coordinate intermediate. The five-coordinate transition state consists of a stable Be-L bond and two stable Be-O bonds; in addition, one stable Be-O bond was replaced by two interactions leading to the breaking of an old and creation of a new Be-O bond.

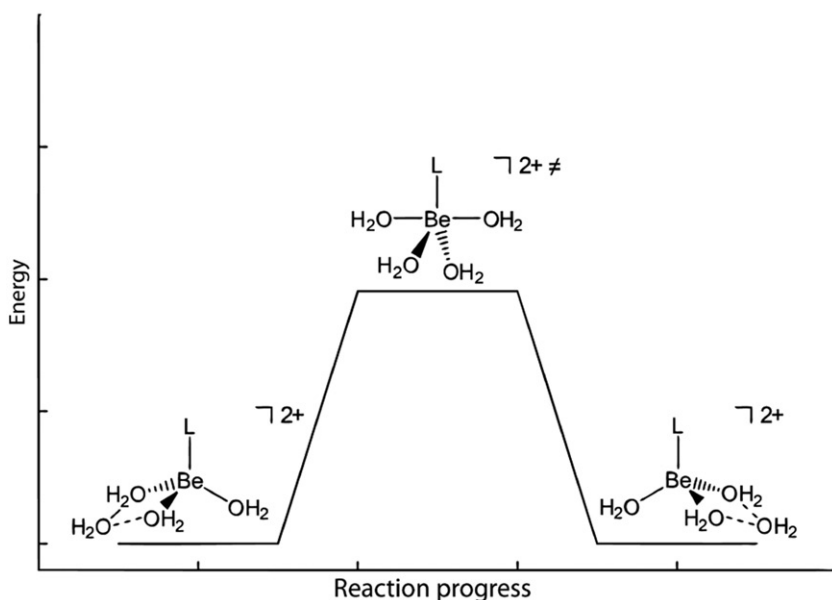


Figure 1. Water-exchange reaction on a  $[\text{Be}(\text{L})(\text{OH}_2)_3(\text{OH}_2)]^{2+}$ -complex (L as described in the text).

The bond length increase between the reactant state's  $\text{Be}-\text{O}_{\text{water}}$  and the transition state's axial  $\text{Be}-\text{O}_{\text{water}}$  bonds is only moderate, characterizing the mechanism as an associative interchange ( $I_a$ ) mechanism (table 1).

Geometries appear to be constant throughout all states. For a particular group of molecules, for example  $\text{NH}_3$ ,  $\text{NH}_2(\text{CH}_3)$ ,  $\text{NH}(\text{CH}_3)_2$ , and  $\text{N}(\text{CH}_3)_3$  or  $\text{SH}_2$ ,  $\text{SH}(\text{CH}_3)$ , and  $\text{S}(\text{CH}_3)_2$ , both bond lengths between  $\text{Be}^{2+}$  and the binding ligand, and between  $\text{Be}^{2+}$  and oxygen remain remarkably constant, generally within 0.05 Å for distances and within  $5^\circ$  for angles (table 1).

However, a small shift can be seen for S, O, and P, where the ligand moves slightly towards  $\text{Be}^{2+}$ . Remarkably, this effect does not occur in N-donor ligands, giving a change in activation energy for  $\text{NH}_x(\text{CH}_3)_{3-x}$ , as discussed further.

As expected, water entering into the second coordination sphere is an exothermic process and leads to an energetically more stable ground state complex (gas phase:  $\sim 25\text{--}30 \text{ kcal mol}^{-1}$ , CPCM:  $\sim 4\text{--}6 \text{ kcal mol}^{-1}$ ) (table 2). In this step, energy differences between MP2 and B3LYP calculations are rather small ( $< 1 \text{ kcal mol}^{-1}$ ) and within the expected range when compared to earlier studies [26]. However, in a solvent, this process is unlikely to happen as a singled out and delayed event. Instead, entrance of water into the second-coordination sphere happens at the same time as coordination of water in the first-coordination sphere. Therefore, this reaction can be considered to be an artifact of gas phase calculations, but allows us to get initial information about the investigated system and its modes of solvation. As expected, energy differences between first- and second coordination sphere complexes calculated using the CPCM solvent model show far smaller energy differences.






Comparing these energies shows a striking similarity between them across all examined complexes, deviating less than  $3 \text{ kcal mol}^{-1}$ . This observation hints towards coordinated ligands not having much, or any, influence on this process.

Table 1. Calculated structural parameters (B3LYP/6-311 + G\*\*).

Distances (Å), angles (°)	Ground state (GS)					Ground state + H <sub>2</sub> O (GS + H <sub>2</sub> O)					Transition state (TS)				
	d Be-O	d Be-L	θ L-Be-O	θ O-Be-O	d Be-O <sub>1CS</sub>	d Be-O <sub>2CS</sub>	d Be-L	θ L-Be-O <sub>1CS</sub>	θ L-Be-O <sub>2CS</sub>	d Be-O <sub>axial</sub>	d Be-O <sub>equatorial</sub>	d Be-L	θ L-Be-O <sub>axial</sub>	θ L-Be-O <sub>equatorial</sub>	
NH <sub>3</sub>	1.67	1.73	112.1	106.8	1.65/1.67	3.34	1.74	108.6/113.2	125.6	2.07	1.66	1.74	96.3	116.0/117.7	
NH <sub>2</sub> CH <sub>3</sub>	1.67	1.71	112.8	105.8	1.66/1.68	3.44	1.72	108.2/114.6	128.3	2.09	1.66	1.72	95.5/97.4	115.2/120.5	
NH(CH <sub>3</sub> ) <sub>2</sub>	1.68	1.71	113.5	105.3	1.66/1.69	3.45	1.72	109.4/ 114.3/ 115.5	128.1	2.09/2.15	1.66	1.73	96.4/100.9	116.6/120.1	
N(CH <sub>3</sub> ) <sub>3</sub>	1.68	1.71	114.1	104.4	1.66/1.69	3.46	1.72	110.4/ 114.9/ 115.7	128.4	2.20	1.65	1.73	101.0/105.6	118.3	
PH <sub>3</sub>	1.67	2.24	112.2	106.6	1.65/1.67	3.42	2.25	109.0/112.7	124.0	2.03	1.66	2.26	96.4	116.5	
PH <sub>2</sub> CH <sub>3</sub>	1.67	2.22	111.7/ 113.1/ 114.5	105.7	1.65/1.68	3.44	2.22	108.5/114.5	127.9	2.06	1.66	2.23	96.7	116.3/119.2	
PH(CH <sub>3</sub> ) <sub>2</sub>	1.68	2.20	112.6/ 114.0/ 114.6	104.9	1.66/1.68	3.46	2.21	108.6/ 114.9/ 116.1	129.2	2.09	1.67	2.22	96.6/98.3	118.6	
P(CH <sub>3</sub> ) <sub>3</sub>	1.68	2.20	114.3	104.1	1.67/1.68	3.47	2.20	110.6/115.4	127.5	2.10	1.67	2.21	98.3	119.4	
AsH <sub>3</sub>	1.66	2.33	112.0	106.9	1.64/1.66	3.41	2.35	108.4/112.6	123.3	2.02	1.66	2.37	95.9	116.0	
AsH <sub>2</sub> CH <sub>3</sub>	1.67	2.32	111.6/ 112.8/ 114.5	106.0	1.66/1.68	3.45	2.32	108.0/114.4	128.0	2.04	1.66	2.34	97.2/94.7	117.7	
AsH(CH <sub>3</sub> ) <sub>2</sub>	1.68	2.30	112.3/ 114.2	104.8	1.65/1.67	3.44	2.33	109.5/114.5	126.3	2.06	1.67	2.33	95.7/97.8	118.5	
As(CH <sub>3</sub> ) <sub>3</sub>	1.68	2.29	114.0	104.3	1.66/1.68	3.47	2.30	110.2/115.3	127.6	2.09	1.67	2.31	98.0	119.3	
OH <sub>2</sub>	1.65	1.65	108.3	110.1	1.64/1.66	3.39	1.66	104.8/ 108.6/ 116.5	127.6	2.00	1.65	1.68	94.3	113.1	
OHCH <sub>3</sub>	1.66	1.62	109.6/ 110.4/ 111.8	106.9/ 108.7/ 109.4	1.65	3.41	1.63	106.3/ 108.8/ 117.8	126.3	2.05	1.65	1.64	95.6	113.2/116.5	
O(CH <sub>3</sub> ) <sub>2</sub>	1.67	1.60	109.4/ 111.5/ 115.2	105.6	1.65/1.68	3.43	1.61	106.9/ 113.6/ 117.0	129.9	2.07	1.65	1.62	95.4	117.8	

(continued)

Table 1. Continued.

	Ground state (GS)					Ground state + H <sub>2</sub> O (GS + H <sub>2</sub> O)					Transition state (TS)				
	d Be-O	d Be-L	θ L-Be-O	θ O-Be-O	d Be-O <sub>1,CS</sub>	d Be-O <sub>2,CS</sub>	d Be-L	θ L-Be-O <sub>1,CS</sub>	θ L-Be-O <sub>2,CS</sub>	d Be-O <sub>axial</sub>	d Be-O <sub>equatorial</sub>	d Be-L	θ Be-L	θ L-Be-O <sub>axial</sub>	θ L-Be-O <sub>equatorial</sub>
SH <sub>2</sub>	1.66	2.33	108.3/ 110.6/	106.9	1.63/1.66	3.40	2.20	104.0/ 108.9/	127.3	1.97/2.02	1.66	2.24	90.2/98.7	114.4	
SHCH <sub>3</sub>	1.60	2.15	115.6 106.2/ 111.0/	106.0/ 106.7/	1.64/1.66	3.40	2.16	109.2/ 110.8/	114.7	2.01	1.66	2.18	90.6/100.0	114.4/116.6	
S(CH <sub>3</sub> ) <sub>2</sub>	1.67	2.12	118.2 105.6/ 113.1/	105.0/108.4	1.65	3.43	2.13	103.5/ 111.5/	133.4	2.04	1.66	2.15	90.5/101.7	116.5	
SeH <sub>2</sub>	1.66	2.33	108.2	106.9/ 107.0/	1.64/1.66	3.40	2.34	105.8/ 109.6/	126.7	1.99/2.03	1.66	2.38	91.6/98.6	114.9	
SeHCH <sub>3</sub>	1.66	2.29	107.7/ 111.5/	105.6/ 106.2/	1.64/1.66	3.41	2.31	109.7/112.5 117.5	117.3	2.03	1.66	2.34	91.3/100.5	114.6/117.2	
Se(CH <sub>3</sub> ) <sub>2</sub>	1.67	2.26	117.9 107.2/ 113.2/	104.9/ 105.2/	1.66	3.34	2.28	111.3/114.4 107.2	116.3	2.05	1.66	2.30	91.1/101.5	117.3	
	1.68	1.68	109.7/117.0	104.4/111.4	1.66/1.69	3.45	1.69	108.4/ 115.0/	131.5	2.06/2.11	1.66	1.70	95.2	118.9	
	1.68	1.68	109.9/116.7	104.5/111.2	1.66/1.69	3.45	1.69	116.5 108.4/ 114.8/	131.7	2.07	1.66	1.69	95.1	118.7	
	1.68	1.68	110.0/116.9	104.4/111.2	1.66/1.69	3.46	1.68	116.6 108.5/ 115.0/	132.1	2.08	1.66	1.69	95.4	118.9	
	1.68	1.67	110.0/117.0	104.3/111.2	1.67/1.69	3.46	1.68	116.7 108.5/ 115.0/	132.3	2.09	1.66	1.69	95.4	119.0	
	1.68	1.67	110.1/117.1	104.2/110.5	1.67/1.69	3.46	1.67	116.6 108.8/ 114.9/	132.9	2.10	1.66	1.68	95.8	119.1	

(continued)



Table 1. Continued.








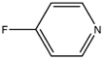
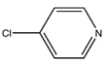
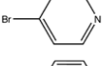
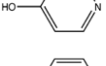
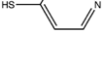
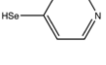
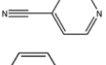
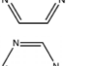
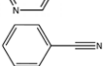

Distances (Å), angles (°)	Ground state (GS)						Ground state + H <sub>2</sub> O (GS + H <sub>2</sub> O)						Transition state (TS)					
	d Be-O	d Be-L	θ L-Be-O	θ O-Be-O	d Be-O <sub>1,CS</sub>	d Be-O <sub>2,CS</sub>	d Be-L	θ L-Be-O <sub>1,CS</sub>	θ L-Be-O <sub>2,CS</sub>	d Be-O <sub>axial</sub>	d Be-O <sub>equatorial</sub>	d Be-L	θ L-Be-O <sub>axial</sub>	θ L-Be-O <sub>equatorial</sub>	d Be-L	θ L-Be-O <sub>axial</sub>	θ L-Be-O <sub>equatorial</sub>	
	1.68	1.66	110.1/117.2	104.1/110.4	1.67/1.69	3.47	1.67	108.7/ 115.2/	132.8	2.10	1.66	1.68	95.8	119.3				
	1.68	1.66	110.1/117.3	104.1/110.9	1.67/1.69	3.47	1.67	108.7/ 115.2/	133.0	2.05	1.66	1.66	94.7	118.7				
	1.69	1.68	109.7/116.4	104.7/ 109.3/ 111.3	1.66/1.69	3.45	1.69	117.1 108.3/ 114.7/ 116.3	131.7	2.07	1.66	1.70	95.2	118.6				
	1.67	1.70	109.4/116.1	105.0/ 109.6/ 111.8	1.66/1.68	3.44	1.71	108.0/ 114.2/ 115.8	130.5	2.07	1.66	1.71	94.9	118.5				
	1.67	1.70	109.6/ 110.8/ 115.2	105.0/ 105.7/ 110.2	1.66/1.68	3.43	1.71	108.4/ 113.3/ 116.1	131.4	2.07	1.66	1.72	95.1	117.5				
	1.67	1.64	112.3/113.8	105.5/107.0	1.66/1.68	3.45	1.65	106.4/ 115.0/ 116.3	128.4	2.05	1.66	1.70	94.7	118.7				
Acetonitrile	1.66	1.67	112.0	107.0	1.65/1.67	3.43	1.68	106.0/114.5	126.8	2.01	1.66	1.70	94.3	117.6				
HCN	1.65	1.71	110.6	108.2	1.64/1.66	3.40	1.72	105.3/112.9	124.4	1.98	1.66	1.74	93.3	116.1				

Table 2. Calculated energies for addition of water into the second-coordination sphere, and the exchange activation energy.

Values (kcal mol <sup>-1</sup> )	GS -> GS + H <sub>2</sub> O			GS + H <sub>2</sub> O -> TS		
	$\Delta E$ B3LYP	$\Delta E$ MP2 (full)	$\Delta E$ B3LYP (CPCM)	$\Delta E$ B3LYP	$\Delta E$ MP2 (full)	$\Delta E$ B3LYP (CPCM)
NH <sub>3</sub>	-28.4	-26.8	-3.6	17.4	18.0	10.5
NH <sub>2</sub> CH <sub>3</sub>	-27.8	-27.9	-3.6	17.6	14.3	10.3
NH(CH <sub>3</sub> ) <sub>2</sub>	-27.3	-27.0	-5.8	19.2	15.8	12.0
N(CH <sub>3</sub> ) <sub>3</sub>	-26.6	-27.0	-5.8	21.1	18.4	15.4
PH <sub>3</sub>	-28.2	-28.3	-4.3	17.6	14.1	9.5
PH <sub>2</sub> CH <sub>3</sub>	-27.2	-27.4	-4.7	17.6	14.3	10.0
PH(CH <sub>3</sub> ) <sub>2</sub>	-26.4	-26.7	-5.4	17.8	14.4	10.3
P(CH <sub>3</sub> ) <sub>3</sub>	-25.9	-26.1	-6.3	18.2	14.4	12.0
AsH <sub>3</sub>	-28.1	-28.1	-4.1	17.5	14.1	10.1
AsH <sub>2</sub> CH <sub>3</sub>	-27.1	-27.2	-4.8	17.9	14.5	11.6
AsH(CH <sub>3</sub> ) <sub>2</sub>	-26.3	-26.5	-4.3	17.8	14.3	9.5
As(CH <sub>3</sub> ) <sub>3</sub>	-25.9	-26.1	-6.6	18.2	14.4	12.4
OH <sub>2</sub>	-29.2	-29.3	-2.5	15.6	9.6	10.3
OHCH <sub>3</sub>	-28.0	-28.3	-3.9	16.2	13.3	9.1
O(CH <sub>3</sub> ) <sub>2</sub>	-27.3	-27.7	-4.6	16.1	12.9	8.8
SH <sub>2</sub>	-29.1	-29.1	-4.3	16.2	12.8	9.3
SHCH <sub>3</sub>	-27.8	-28.1	-4.7	17.5	13.9	10.0
S(CH <sub>3</sub> ) <sub>2</sub>	-26.6	-27.0	-6.1	16.8	13.1	10.7
SeH <sub>2</sub>	-28.8	-28.7	-4.1	18.3	17.3	16.3
SeHCH <sub>3</sub>	-27.7	-27.9	-4.6	17.5	13.9	10.0
Se(CH <sub>3</sub> ) <sub>2</sub>	-26.6	-26.8	-5.0	17.4	13.7	9.8
	-25.6	-26.3	-3.7	15.5	11.9	9.2
	-25.9	-26.6	-3.8	15.6	12.0	8.9
	-25.5	-26.3	-3.9	15.4	11.8	9.1
	-25.4	-26.2	-3.9	15.4	11.7	9.1
	-25.0	-25.8	-3.7	15.5	12.1	9.3
	-24.8	-25.6	-3.8	15.3	11.9	9.3
	-24.6	-25.5	-3.7	15.1	11.6	9.2
	-26.2	-25.2	-3.9	15.6	11.6	8.9
	-26.7	-27.3	-4.0	15.6	11.9	8.5
	-27.5	-28.1	-4.3	15.9	12.2	9.1
	-24.8	-25.5	-3.9	15.9	12.0	9.2
Acetonitrile	-27.9	-28.0	-3.8	16.1	12.4	8.6
HCN	-26.4	-26.7	-3.7	16.5	12.8	9.2

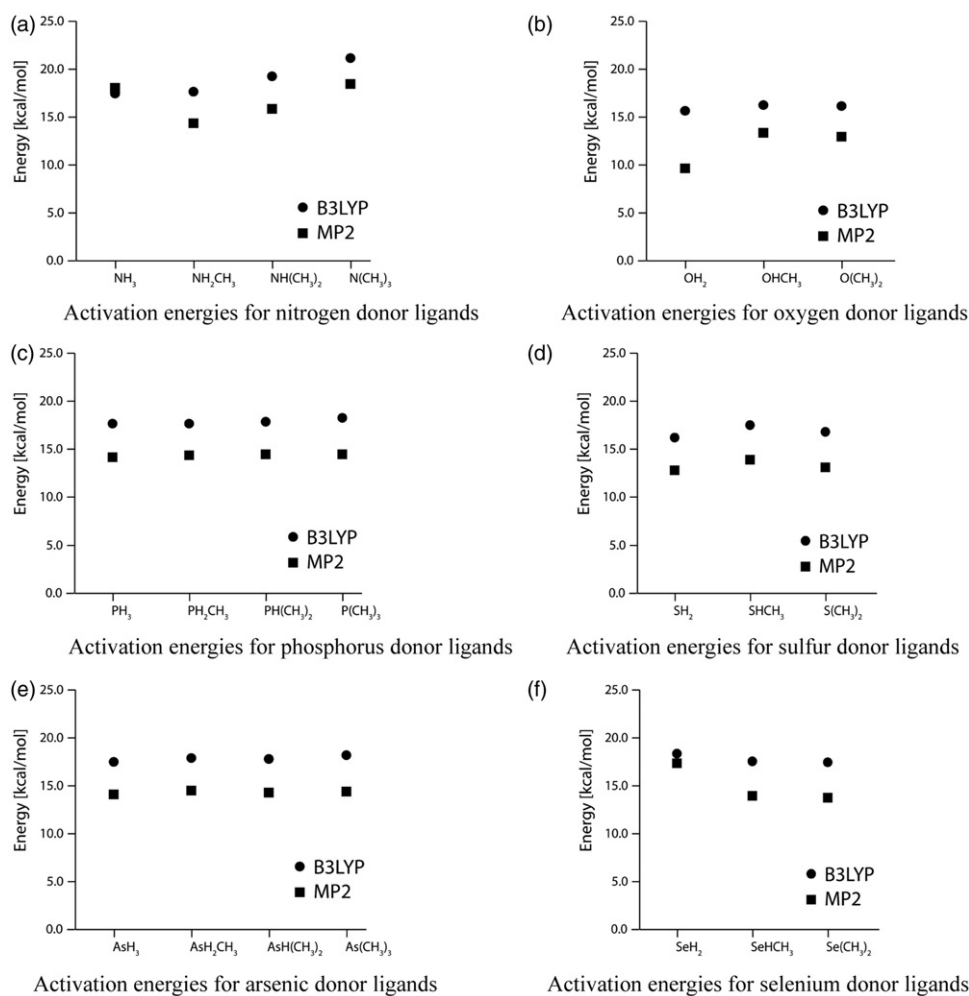


Figure 2. Calculated (B3LYP/6-311+G\*\*) activation energies for the water-exchange reaction at  $[\text{Be}(\text{L})(\text{OH}_2)_3(\text{OH}_2)]^{2+}$ .

The second calculated reaction step shows exchange of a second-coordination sphere water with the one from the first coordination sphere (table 2). Activation energies of this reaction for the examined ligands are plotted in figure 2(a–h).

As can be seen, gas phase activation energy differences are negligibly small, with the exception of nitrogen  $\text{sp}^3$  ligands  $\text{NH}_3$ ,  $\text{NH}_2(\text{CH}_3)$ ,  $\text{NH}(\text{CH}_3)_2$ , and  $\text{N}(\text{CH}_3)_3$ , which, as mentioned above, show a significant but small increase in activation energy with increasing number of methyl substituents. This series will be examined closer in the next paragraph.

For all other ligands, differences in activation energies are below  $3 \text{ kcal mol}^{-1}$  overall, and below  $2 \text{ kcal mol}^{-1}$  within one series of ligands, and therefore close to the level of significance. Comparison of the three applied quantum chemical methods shows for MP2 the well-known and well-documented underestimation of activation energies [28], while the CPCM values are  $2/3$  of the B3LYP values. This observation is in line with previous

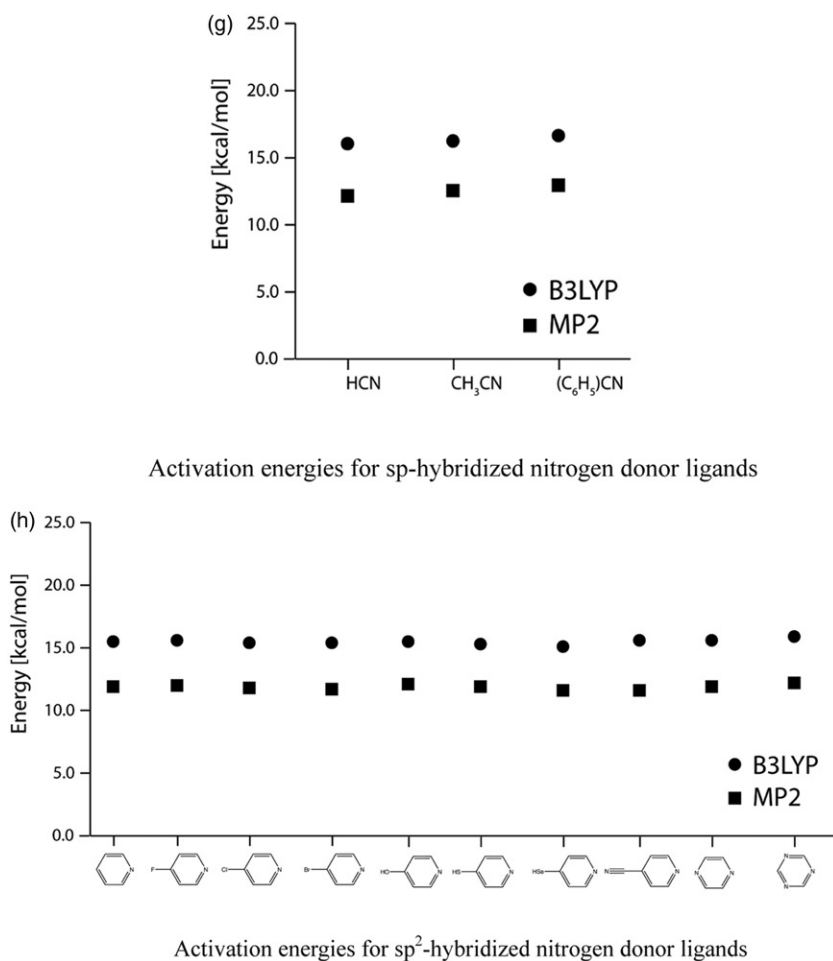


Figure 2. Continued.

findings for CPCM calculations in the implementation of Gaussian 03, applying default settings [29, 30]. These small energy differences again point towards a weak or nonexistent influence of L on the coordination of water and lead to the conclusion that most of these ligands are spectator ligands. Keeping the tetrahedral geometry of these complexes in mind, this behavior can be rationalized within the missing *trans*-influence that would be present in octahedral or trigonal-bipyramidal complexes [31–33].

As a test case, we switched the roles between the ligand and the solvent for HCN and calculated the HCN exchange reaction for  $[\text{Be}(\text{HCN})(\text{H}_2\text{O})_3]^{2+}$  (12.6 kcal mol<sup>-1</sup>),  $[\text{Be}(\text{HCN})_2(\text{H}_2\text{O})_2]^{2+}$  (12.1 kcal mol<sup>-1</sup>),  $[\text{Be}(\text{HCN})_3(\text{H}_2\text{O})]^{2+}$  (14.5 kcal mol<sup>-1</sup>), and  $[\text{Be}(\text{HCN})_4]^{2+}$  (11.7 kcal mol<sup>-1</sup>). As expected, the differences in activation energies between these complexes are very small, below 3 kcal mol<sup>-1</sup>, therefore proving spectator status of the nonexchanging ligand.

However, as already reported, activation energies decrease with decreasing p-orbital participation in the solvent molecule's coordinating electron pair. In addition, comparison between these calculations and water exchange on  $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$  shows a

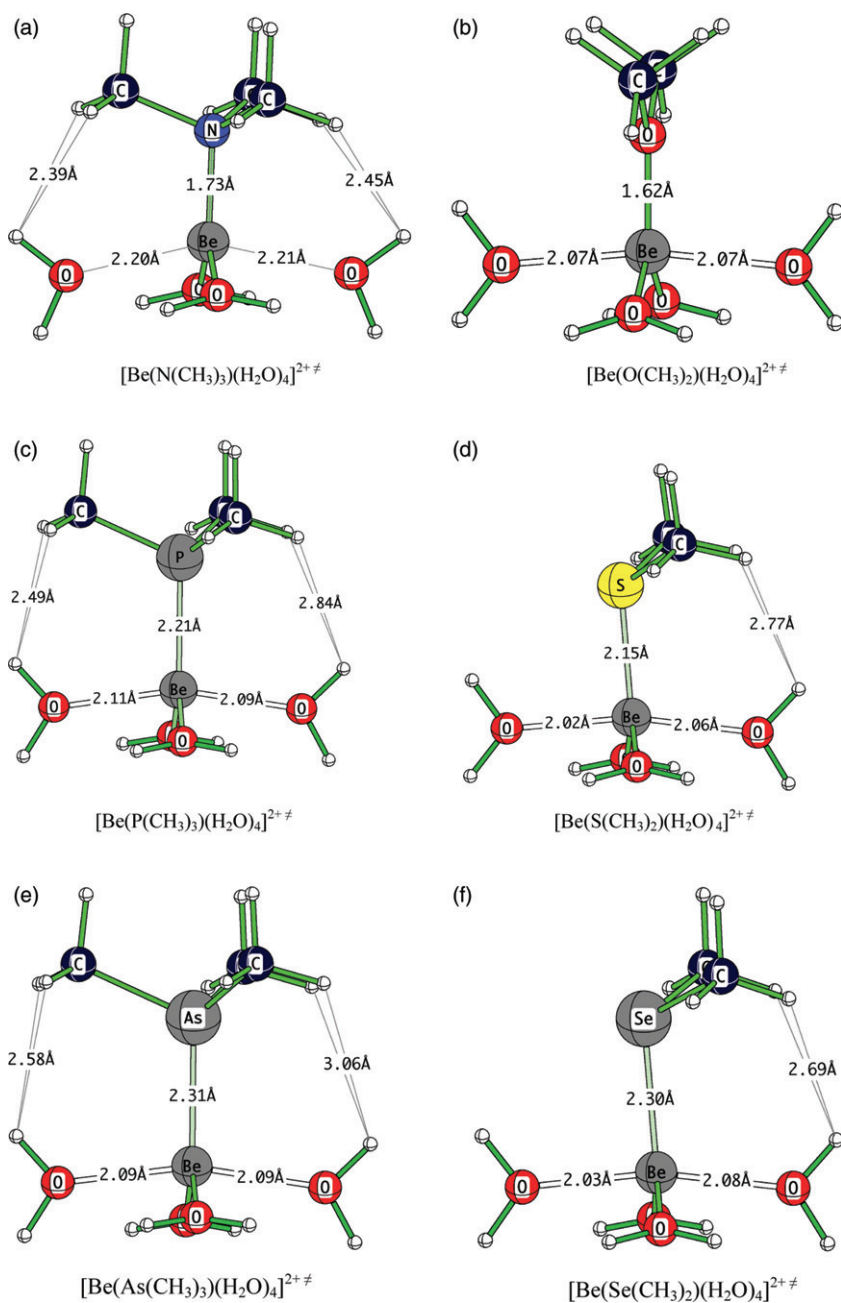


Figure 3. Structures of the calculated (B3LYP/6-311 + G\*\*) transition states for  $[\text{Be}(\text{L})(\text{OH}_2)_4]^{2+ \neq}$  (here for pemethylated derivatives of L).

solvent influence larger than the ligand influence on this reaction. This is due to the trigonal bipyramidal geometry of the transition state, in which the two axial ligands, in this case the exchanging water molecules, can exert a *trans*-labilizing effect on each other. See figure 3 for an example of this configuration.

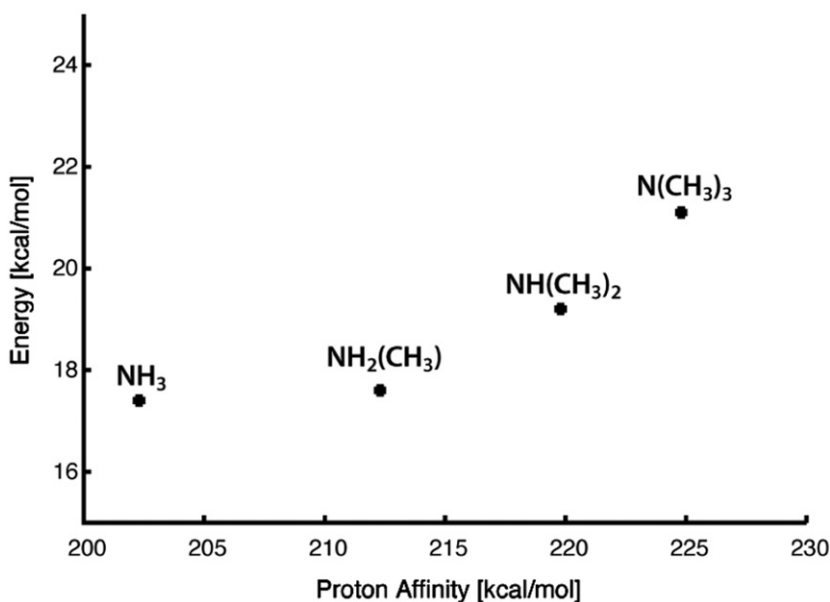


Figure 4. Calculated (B3LYP/6-311 + G\*\*) activation energy vs. calculated (B3LYP/6-311 + G\*\*) proton affinity for  $N(H)_x(CH_3)_{3-x}$ .

Mechanistically, all examined reactions show an associative interchange mechanism, consistent with the observed ligand spectator status and the missing *trans*-effect on almost all examined ligands. Otherwise, either of these effects alone would likely lead to a change in mechanism within the different complexes.

Examining the group of ammonia and amine ligands, an increase in activation energy from ammonia to trimethylamine is observed. Through electron donation effects of the methyl groups, the ability to donate electrons, and therefore the gas phase proton affinity, increases [34]. This stems from an increase in electron density on nitrogen, resulting from stronger electron donation that methyl groups show relative to protons, increasing the total electron donation with the number of attached methyl groups. This, in turn, decreases the nitrogen's local softness due to the outward push of the increased electron density, as discussed by Torrent-Sucarrat *et al.* [31], and gives a correlation between activation energy and local softness. However, no such correlation could be found for oxygen, phosphorus, or sulfur ligands when using data from the same source [31].

In most cases, higher electron density on a ligand leads to increased electron donor capability, thus raising electron density on the coordination center. If the coordination center is a hard acid like  $Be^{2+}$ , this would make a nucleophilic attack by water more difficult on this center. This behavior is confirmed by our calculations (figures 4 and 5).

As mentioned above, the correlation found for N  $sp^3$ -ligands does not occur for O, P, or S  $sp^3$ -ligands. This can be attributed to a steric effect of the nitrogen ligands. Proof for this steric hindrance can be seen in L-Be shortening with increasing methylation for O, P, and S donor ligands, which does not exist for the examined N-donor ligands.

The examined  $sp$  and  $sp^2$ -ligands show no correlation between activation energy and any other parameter. Compared to the  $sp^3$  ligands, the activation energy is generally

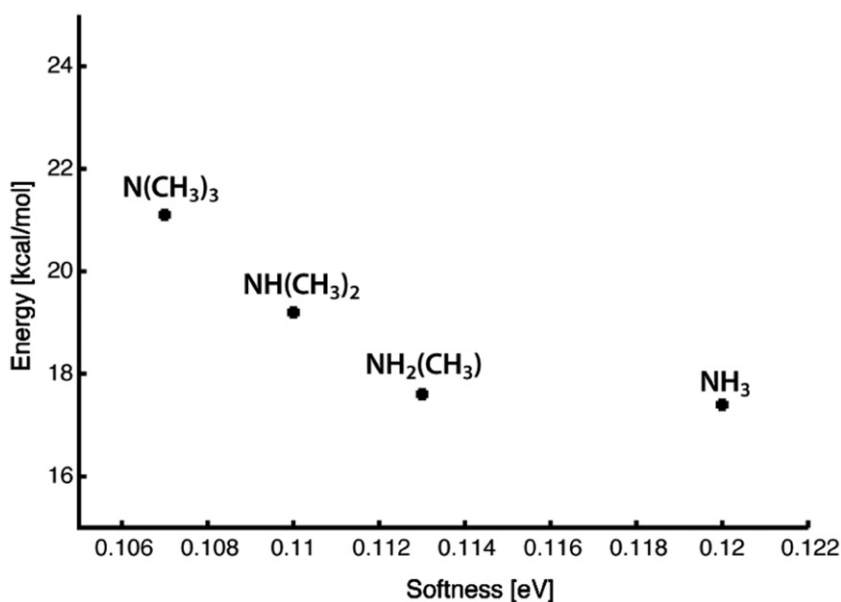


Figure 5. Calculated (B3LYP/6-311+G\*\*) activation energy vs. softness [31] for  $\text{N}(\text{H})_x(\text{CH}_3)_{3-x}$ .

lower, which we attribute to raised s-contribution in  $\text{sp}^2$ - and  $\text{sp}$ -hybrid orbitals as compared to  $\text{sp}^3$ .

Within the group of  $\text{sp}$  ligands, both HCN and  $\text{CH}_3\text{CN}$  have a lower activation energy, attributable to their weaker mesomeric stabilization, compared to the benzene ring system in  $\text{C}_6\text{H}_5\text{CN}$ .

### 3. Conclusion

Our results show conclusively that water-exchange reactions on beryllium complexes of the type  $[\text{Be}(\text{L})(\text{H}_2\text{O})_3]^{2+}$ , involving neutral ligands  $\text{NH}_{3-x}(\text{CH}_3)_x$ ,  $\text{PH}_{3-x}(\text{CH}_3)_x$ ,  $\text{AsH}_{3-x}(\text{CH}_3)_x$ ,  $\text{OH}_{2-x}(\text{CH}_3)_x$ ,  $\text{SH}_{2-x}(\text{CH}_3)_x$ ,  $\text{SeH}_{2-x}(\text{CH}_3)_x$ , pyridine, 4-fluoropyridine, 4-bromopyridine, 4-chloropyridine, 4-hydroxypyridine, 4-thiopyridine, 4-selenidopyridine, 4-nitriropyridine, 1,4-diazine, 1,3,5-triazine, HCN, acetonitrile, and benzonitrile, follow an associative interchange mechanism throughout. Unlike the other examined ligands, nitrogen donors exhibit a correlation between donor strength, expressed by the donor's local softness, and the water-exchange activation energy, whereas all other  $\text{sp}^3$  ligands keep their activation energy virtually constant while their L-Be distance varies. We attribute this difference to a steric effect in  $\text{sp}^3$ -N-donor ligands preventing a similar bond-shortening effect, which leads to a variation in activation energy as substituent effect. Therefore, all but the  $\text{sp}^3$ -N-donor ligands are in fact, as shown by the example for HCN, spectator ligands due to a missing donor *trans*-influence in both the tetrahedral ground state and the trigonal-bipyramidal transition state geometries.

#### 4. Quantum chemical methods

All structures were fully optimized at the B3LYP/6-311+G\*\* [35, 36] level and characterized by the computation of vibrational frequencies. Following a remark by Schreiner *et al.* [37], gas phase reaction energies were evaluated by MP2(full)/6-311+G\*\* single point calculations (all electrons were included in the correlation treatment) [38, 39] of our B3LYP/6-311+G\*\*-optimized geometries. In an earlier study, we proved that the obtained MP2(full)/6-311+G\*\*//B3LYP/6-311+G\*\*+ZPE (B3LYP/6-311+G\*\*) results are nearly identical to those of so called high accuracy methods (G1, G2, and G3) [26]. The influence of bulk solvent was probed by single point calculations using the CPCM formalism [40–42] with water as solvent, i.e., B3LYP (CPCM:H<sub>2</sub>O)/6-311+G\*\*//B3LYP/6-311+G\*\*+ZPE (B3LYP/6-311+G\*\*). All calculations were performed using Gaussian 03 [43]. The gas phase proton affinities were calculated for 0 K following the approach of Raabe *et al.* [44, 45] at B3LYP/6-311+G\*\* including ZPE correction.

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