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**Ligand Exchange Processes on Solvated Zinc Cations.
 DFT Analysis of Hydrogen Cyanide Exchange on
 [Zn(HCN)₆]²⁺**

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Keywords:	HCN exchange, Density functional calculations, Zinc, Coordination chemistry



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3 Sehr geehrter Herr Prof. Jansen,
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6
7 anbei finden sie unser überarbeitetes Manuskript zaac.200900160 ("Ligand Exchange
8 Processes on Solvated Zinc Cations. DFT Analysis of Hydrogen Cyanide Exchange on
9 [Zn(HCN)₆]²⁺") und unsere Antworten auf die Anmerkungen der Gutachter.
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14 Wir hoffen, dass unser Manuskript in der jetzigen Form geeignet ist für ZAAC.
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16

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18 Mit freundlichen Grüßen
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21 Ralph Puchta
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23

24
25 Reviewer: 1

26
27 Comments to the Author

28 This is sound but exclusively affirmative theoretical work. It is an editorial decision
29 whether such results are compatible with the profile of ZAAC.
30

31 The authors make repeatedly clear that the results are just supportive, confirming "once
32 again" the character of HCN as water-like, the mechanistic preference as with other metal
33 ions, the role of charge and size.
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36 I consider the work acceptable if the parts dealing with those trivial aspects are
37 significantly condensed, and if more interesting aspects e.g. on H bonding or on Zn
38 coordination ambivalence are being discussed.
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44 We shortened the aspect of HCN as a water-like solvent and focused more on H-bonding,
45 as suggested. Parallel we stressed our original intention more to correct the wrong
46 published mechanism. With respect to Prof. Wasada-Tsutsui we did not point this out so
47 directly before, but with the Reviewer 1's encouragement we added a few sentences.
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53 The reference choice in the introduction is curious; organozinc compounds cannot be
54 seriously considered as models. Instead, Vahrenkamp's or RJP Williams' characterisation
55 of Zn(2+) is recommended for citation.
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3 Personally we are a little bit surprised, that Reviewer 1 detected organozinc compounds
4 in our literature. Since we assume that Reviewer 1 relies on Lit [8] (Z. Rappoport, I.
5 Marek, *The Chemistry of Organozinc Compounds*) and other readers could get the same
6 impression, we extended the citation to:
7
8
9

10 [1] G. Schürer, T. Clark, R. van Eldik “The reaction mechanisms of zinc enzymes” in Z.
11 Rappoport, I. Marek, *The Chemistry of Organozinc Compounds*, Chap. 1, Part 1, John
12 Wiley & Sons Ltd, England, (2006).
13
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18 We totally agree that the work by Vahrenkamp and RJP Williams has to be cited, and we
19 have corrected this.
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23 Reviewer: 2

24 Comments to the Author

25 The authors study the ligand exchange mechanism in $[\text{Zn}(\text{HCN})_6]^{2+}$ by DFT methods.
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27 All the structures and energies have been evaluated in the gas phase.
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31 Major concerns:
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35 1. Although the authors allegedly aim at studying the processes that metal cations
36 undergo in solutions, they have limited themselves to the gas-phase calculations only.
37 The complexes are highly charged (overall charge +2) and the solvation effects,
38 especially in such high dielectric medium as liquid HCN, are expected to be quite
39 substantial and may alter the gas-phase reaction pathway. Therefore, the authors should
40 evaluate thermodynamic parameters for the respective reactions in the condensed media
41 before making definitive conclusions about the reaction mechanism.
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49 The appropriate consideration of solvent effects is still a challenging task. On the one
50 hand there are very crude implicit solvent models, but on the other hand one can apply *ab*
51 *initio* molecular dynamic simulations. While the latter give good and reliable results, they
52 are very expensive/computer time consuming. The implicit solvent models like CPCM,
53 IPCM etc. are fast and easily available, but very crude and tend to collapse in many
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3 cases. As we did not want to bore our readers with too much detail, we did not mention in
4 the submitted document that we tried to evaluate all stationary points at least by single
5 point calculations with such implicit solvent models. Sadly, one calculation failed. As
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8 expected from earlier similar studies, the parts of the presented reactions that we could
9 evaluate did not show any significant difference from the presented (gas phase) data.
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14 2. Entropic effects are not expected to be negligible either and should be taken into
15 account too. Thus, free energies, instead of reaction energies should be evaluated.
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19 We did not calculate entropic contributions for the following reasons: Entropic effects are
20 hardly manageable in such reactions. The entering solvent comes from the bulk and the
21 leaving solvent again goes to the bulk. Therefore fair equations that will lead to
22 comparable results are a problem. As in a related study (ChemPhysChem 2007, 8, 1315 –
23 1320) we inspected this question for free energies and did not find significant
24 improvements, and to obtain comparable results with former studies we applied the
25 concept of M. Hartmann, T. Clark, R. van Eldik, *J. Am. Chem. Soc.* **1997**, *119*, 5867.
26 We are convinced that only *ab initio* molecular dynamic simulations offer the chance to
27 consider entropic and solvent effects in a reasonable way. For this and the above
28 mentioned reasons we plan to extend our studies in the direction of *ab initio* molecular
29 dynamic simulations, but this is a question of available resources.
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40 Minor issues:
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44 It is not quite clear to the reader what the purpose/motivation/usefulness of this study is.
45 It will be beneficiary for the paper if the authors could elaborate more on this issue and
46 outline the significance of their findings.
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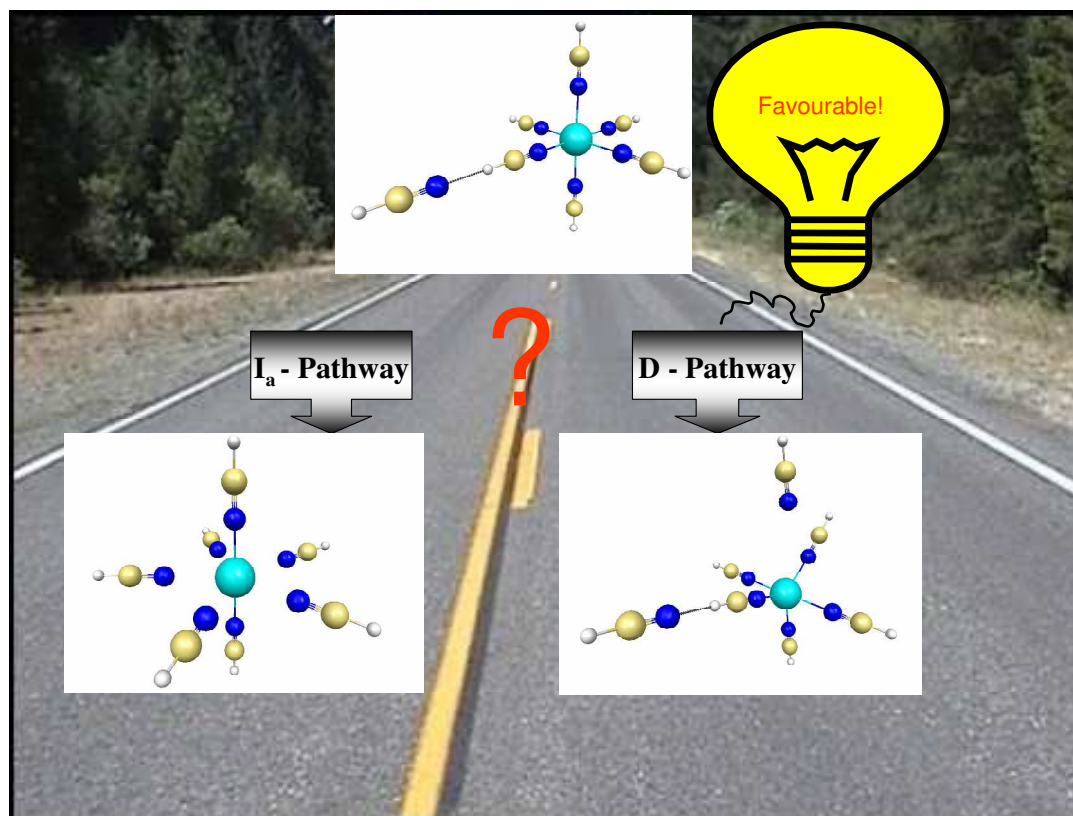
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51 We improved this as described in the response to Reviewer 1.
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Synopsis

Ligand Exchange Processes on Solvated Zinc Cations. DFT Analysis of Hydrogen Cyanide Exchange on $[\text{Zn}(\text{HCN})_6]^{2+}$

Basam M. Alzoubi, Ralph Puchta* and Rudi van Eldik*

Possible mechanisms for hydrogen cyanide exchange on $[\text{Zn}(\text{HCN})_6]^{2+}$ were studied using density functional theory (B3LYP/6-311+G**). The computed structural parameters and activation energies show that the activation barrier for a limiting dissociative (D) mechanism (7 kcal mol⁻¹) is clearly more favorable than for an associative interchange (I_a) mechanism (15.9 kcal mol⁻¹). HCN exchange exhibits a limiting dissociative mechanism similar to that found for water exchange on $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$. The results support the classification of HCN as a water-like solvent.



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3 **Ligand Exchange Processes on Solvated Zinc Cations -**
4 **DFT Analysis of Hydrogen Cyanide Exchange on $[\text{Zn}(\text{HCN})_6]^{2+}$**
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8 Basam M. Alzoubi,^{a,b} Ralph Puchta,^{a,c*} and Rudi van Eldik^{a*}
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11 *Dedicated to Professor Lutz Dahlenburg on the Occasion of his 65th Birthday*
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16 **Keywords:**

17 HCN exchange; Density functional calculations; Zinc; Coordination chemistry
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23 **Abstract:**

24 The mechanisms for hydrogen cyanide exchange on $[\text{Zn}(\text{HCN})_6]^{2+}$ were studied using
25 density functional theory (B3LYP/6-311+G**), and showed that the limiting dissociative
26 (D) pathway is more favorable than the associative interchange (I_a) mechanism. The
27 activation barrier for the dissociative mechanism (7 kcal mol⁻¹) is clearly lower than for
28 the interchange mechanism (15.9 kcal mol⁻¹).
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Introduction:

Zinc is the second most abundant transition metal in living organisms and plays a very important role in structural and reactive biochemical processes, viz. it is involved in nucleic acid binding and gene regulation [1]. It shows six-fold coordination with small solvent molecules like water or acetonitrile [2]. In zinc-finger proteins and enzymes, zinc is usually tetrahedrally coordinated, but in some catalytic binding sites it is found to be five-coordinate and rather rarely as six-coordinate [3]. Divalent zinc coordinates to hard and soft ligands present in metalloenzymes due to its flexible coordination geometry, lack of redox activity, intermediate polarizability, and being on the borderline of the hard-soft character [4]. In the case of model complexes, it can form four-, [5] five-, [6] and six-coordinate [7] complexes, which is dictated by the ligand size, structure and charge [8].

Water exchange reactions, or solvent exchange reactions in a more general sense, are the most fundamental substitution processes that a metal ion in solution can undergo. There are three simple mechanistic pathways for solvent exchange: (i) the limiting dissociative (D) process with an intermediate of lower coordination number; (ii) the limiting associative (A) process with an intermediate of higher coordination number; (iii) the interchange (I) process, in which no intermediate is involved and the exchange occurs in a concerted manner. The interchange process can be more dissociative (I_d) or more associative (I_a) in nature, depending on whether bond breakage or bond formation is more important, respectively. For the interchange mechanisms, the reactants have been suggested to form a precursor-complex prior to the rate-determining interchange step [9]. The present understanding of solvent exchange mechanisms is largely based on volume of activation (ΔV^\ddagger) data measured for such processes [10]. For this purpose much development has gone into high-pressure NMR techniques in order to determine exchange rate constants as a function of pressure up to 300 MPa [11].

The water exchange mechanism of hydrated zinc(II) was studied theoretically by Hartmann et al. [12,13] Structures and hydration energies were calculated using hybrid density functional theory (DFT) for $[\text{Zn}(\text{H}_2\text{O})_n]^{2+}$ with $n = 1-6$ and for

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3 $[\text{Zn}(\text{H}_2\text{O})_n \cdot m\text{H}_2\text{O}]^{2+}$ where $n = 5, m = 1, 2$; $n = 6, m = 1$; and $n = 3-6, m = 0-2$ where n
4 and m represent the number of water molecules in the coordination and solvation spheres,
5 respectively. On the basis of structures and energies, the water exchange mechanism for
6 $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ was found to be a limiting D mechanism and the results are in good
7 agreement with ab initio calculations and self-consistent reaction field methods [14].
8 Beside the work by Hartmann et al., a solvent exchange study by Wasada-Tsutsui et al.
9 [15] suggested for the water like solvent HCN,[16] based on quantum chemical
10 calculations, an associative HCN exchange at $[\text{Zn}(\text{HCN})_6]^{2+}$ without providing any
11 mechanistic details.
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21 Recently, we showed on the basis of quantum chemical calculations that water and HCN
22 exchange on $[\text{Li}(\text{S})_4]^+$, [17,18] $[\text{Be}(\text{S})_4]^{2+}$ [19] and $[\text{Al}(\text{S})_6]^{3+}$ [20,21] ($\text{S} = \text{H}_2\text{O}, \text{HCN}$)
23 show the same type of mechanism. The exchange mechanism for solvated Li^+ is of the
24 limiting associative (A) type, for solvated Be^{2+} of the interchange (I) type, and solvated
25 Al^{3+} follows a limiting dissociative (D) mechanism. Based on this analogy between the
26 water and hydrogen cyanide exchange mechanisms, we expect on the basis of
27 Hartmann's work a dissociative solvent exchange process for Zn^{2+} in contrast to the
28 finding of Wasada-Tsutsui et al. [15]. This aspect has therefore been studied in more
29 detail in the present study.
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38 **Quantum chemical methods**

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40 Following the suggestions of Hartmann et al., [13] and for comparison with recent studies
41 on solvent exchange at Li^+ , [17,18,22] Be^{2+} , [19,23] and Al^{3+} , [20,21] we fully optimized
42 the structures at the B3LYP/6-311+G** level of theory [24] and characterized by
43 computation of vibration frequencies the structures as local minima or transition states.
44 The Gaussian 03 suite of programs was used throughout [25].
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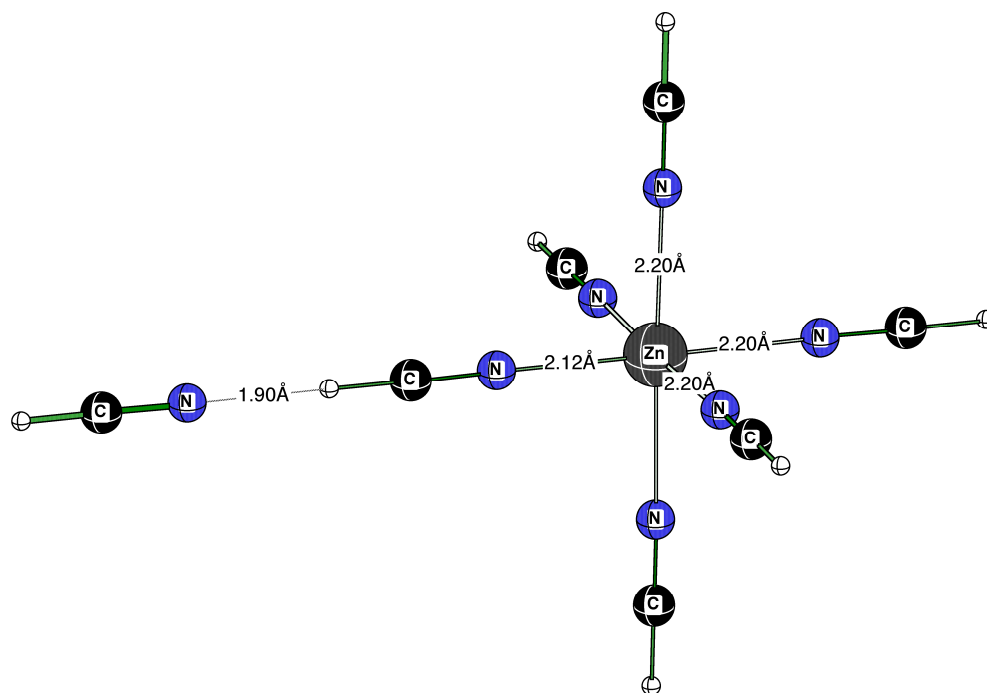
51 **Results and Discussion**

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55 The reactant, transition and intermediate states were calculated for hydrogen cyanide
56 exchange. The computed data offered two transition states for limiting dissociative and
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3 associative interchange exchange mechanisms. In the present work, the two mechanisms
4 were studied in more detail using structural parameters and activation energies to
5 pinpoint the more favorable mechanism.
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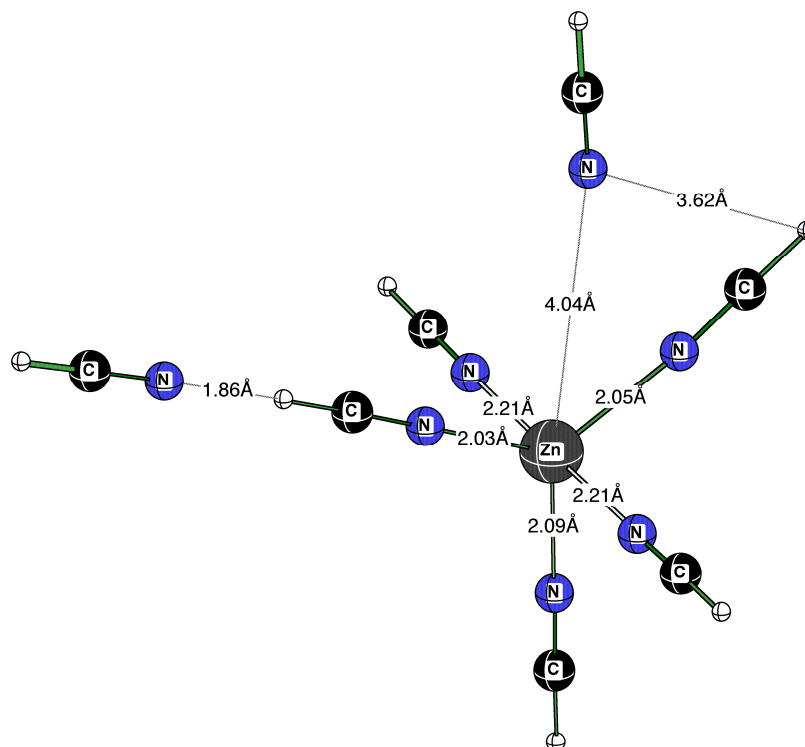
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11 **Limiting dissociative mechanism:**

12 Both reaction pathways start at $[\text{Zn}(\text{HCN})_6\cdot\text{HCN}]^{2+}$ as reactant state. As depicted in
13 Figure 1, the reactant has one hydrogen cyanide molecule in the second coordination
14 sphere bound by a single hydrogen bond of 1.90 Å to one of the hydrogen cyanide
15 molecules in the first coordination sphere of C_4 symmetric $[\text{Zn}(\text{HCN})_6\cdot\text{HCN}]^{2+}$.
16 Detaching one of the coordinated hydrogen cyanide molecules leads to the transition state
17 for the limiting dissociative mechanism (see Figure 2). In the transition state the HCN-
18 Zn^{2+} interaction is broken and a hydrogen bond with one of the coordinated HCN in the
19 first coordination shell is formed, leading to a five-coordinate Zn^{2+} ion as intermediate. In
20 this structure, the leaving HCN molecule becomes part of the second coordination sphere
21 and forms a hydrogen bond with a HCN molecule in the first coordination sphere of 1.85
22 Å and in parallel the hydrogen bonded HCN of the first coordination sphere is bound
23 more tightly (see Figure 3). The distance between the leaving HCN molecule and the
24 central metal atom is 4.04 and 6.14 Å in the transition and intermediate states,
25 respectively. On the other hand, the hydrogen bond distance is 3.62 and 1.85 Å,
26 respectively. The coordination sphere changes from an octahedral, via a distorted
27 trigonal-bipyramidal in the transition state, to a symmetric trigonal-bipyramidal structure
28 for the five-coordinate intermediate.
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Figure 1. Calculated structure (RB3LYP/6-311+G**) of the reactant state $[\text{Zn}(\text{HCN})_6 \cdot \text{HCN}]^{2+}$.



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Figure 2. Calculated structure (RB3LYP/6-311+G**) of the transition state $[\text{Zn}(\text{HCN})_5 \cdot 2\text{HCN}]^{2\ddagger}$.

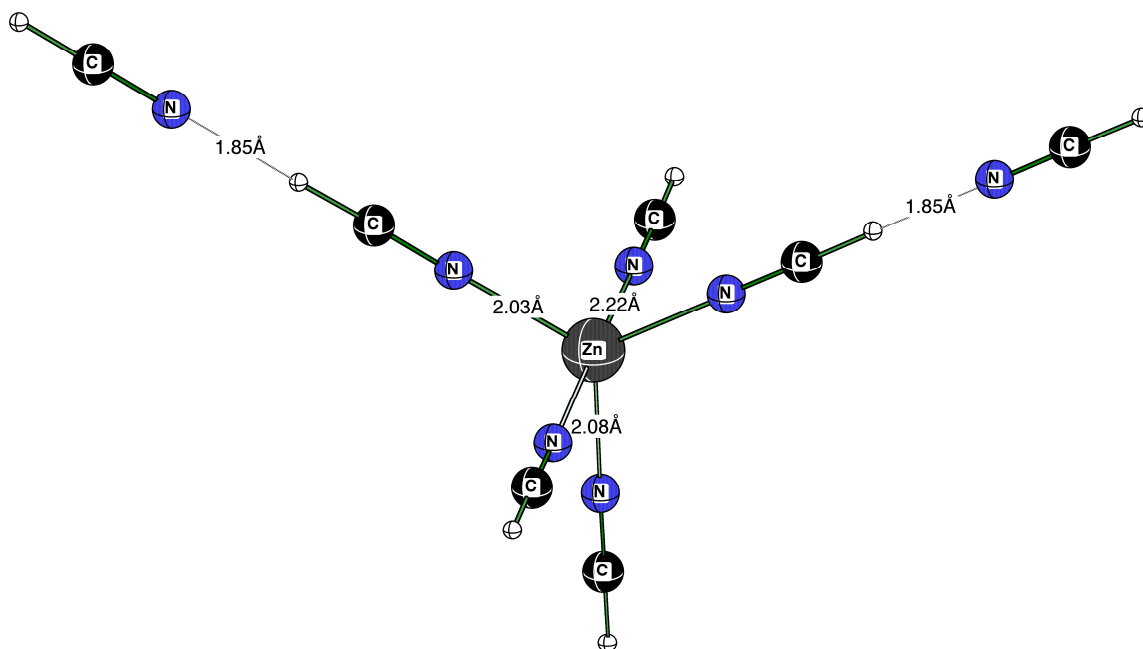


Figure 3. Calculated structure (RB3LYP/6-311+G**) of the five-coordinate intermediate $[\text{Zn}(\text{HCN})_5 \cdot 2\text{HCN}]^{2+}$.

Associative interchange mechanism:

The C_2 symmetric transition state of the associative interchange (I_a) mechanism contains two weakly coordination (2.41 \AA) exchanging hydrogen cyanide molecules (see Figure 4) [26]. Starting from $[\text{Zn}(\text{HCN})_6 \cdot \text{HCN}]^{2+}$, the second sphere hydrogen bonded HCN molecule moves into the first coordination sphere and weakens the Zn-NCH bond of the *cis* standing HCN molecule, which is released during the exchange process. The Zn-N bond lengths of the reactant state are significantly shorter than in the case of the transition state of the I_a mechanism (see Figures 1 and 4). The first coordination sphere changes from an octahedral structure in the reactant to a distorted pentagonal-bipyramidal structure in the transition state. The entering HCN molecule has come significantly close to the Zn(II) center in the transition state for the mechanism to be classified as associative interchange (I_a).

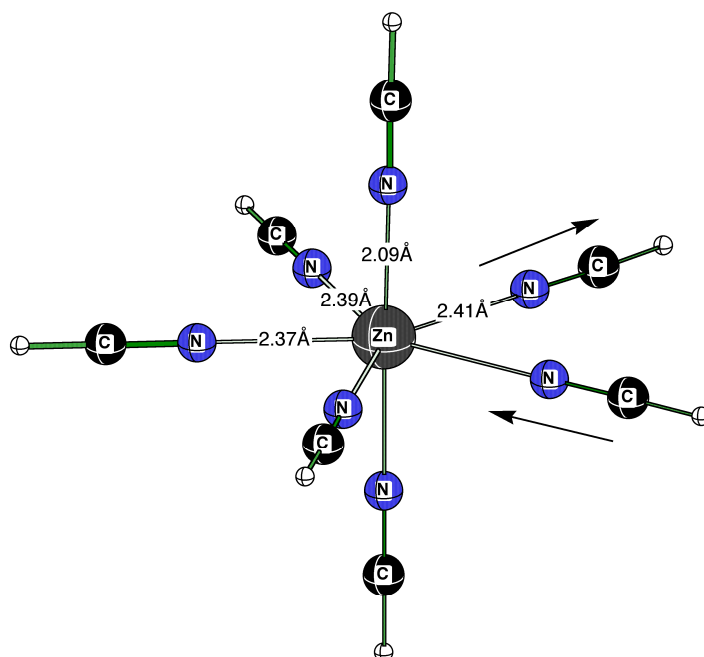
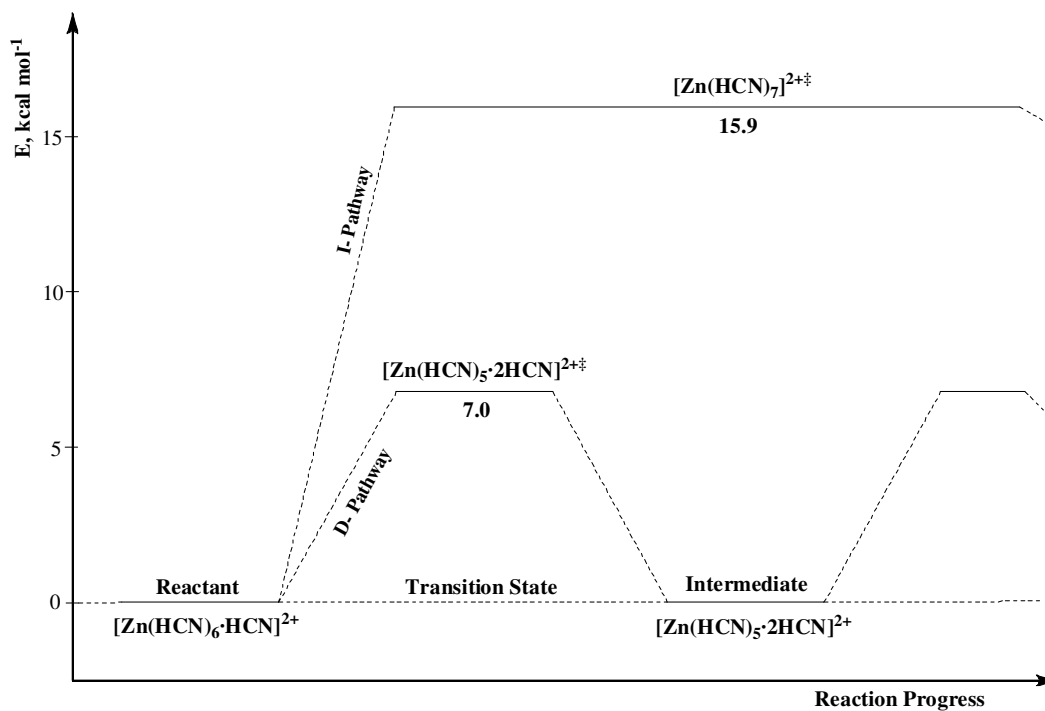


Figure 4. Calculated structure (B3LYP/6-311+G**) of the transition state $[\text{Zn}(\text{HCN})_7]^{2+\ddagger}$.

Attribution of the mechanism:

A comparison of the activation barriers shows that the limiting dissociative pathway is clearly favored since lies $8.9 \text{ kcal mol}^{-1}$ lower in energy than the transition state of the associative interchange mechanism (see Scheme 1). We attribute the difference in stability between the two transition states to bond weakening of the five equatorial HCN ligands in $[\text{Zn}(\text{HCN})_7]^{2+\ddagger}$ which are elongated by 0.2 \AA with respect to the ground state $[\text{Zn}(\text{HCN})_6 \cdot \text{HCN}]^{2+}$. Whereas the equatorial ligands undergo only smaller changes in the limiting dissociative transition state, three of the five coordinated HCN ligands in $[\text{Zn}(\text{HCN})_5 \cdot 2\text{HCN}]^{2+\ddagger}$ are bound even more tightly than in the ground state. The five-coordinate intermediate of the limiting dissociative mechanism, $[\text{Zn}(\text{HCN})_5 \cdot 2\text{HCN}]^{2+}$, is as stable as the ground state reactant complex $[\text{Zn}(\text{HCN})_6 \cdot \text{HCN}]^{2+}$.



Scheme 1. Calculated (B3LYP/6-311+G**) energy profile for HCN exchange on $[\text{Zn}(\text{HCN})_6]^{3+}$ according to limiting dissociative (D) and associative interchange (I_a) reaction pathways.

As mentioned above, the bond lengths in the transition state $[\text{Zn}(\text{HCN})_7]^{2+\ddagger}$ are clearly longer and the metal-ligand interactions are therefore weaker than in the case of $[\text{Zn}(\text{HCN})_5 \cdot 2\text{HCN}]^{2+\ddagger}$ (see Table 1). Rotzinger[14,27] suggested as a quantum-chemical descriptor for the activation volume that the sign of the change of the sum of all M-ligand bond lengths ($\Delta\Sigma$) during the activation process should agree with the sign of ΔV^\ddagger . In accordance with the expected trend, the calculated change in the Zn-N bond lengths during the exchange reaction ($\Delta\Sigma$) were found to be positive for the limiting dissociative mechanism and negative for the associative interchange mechanism (see Table 1). In addition, Σr_3 increases significantly on going from the transition state, $[\text{Zn}(\text{HCN})_5 \cdot 2\text{HCN}]^{2+\ddagger}$, to the five-coordinate intermediate, $[\text{Zn}(\text{HCN})_5 \cdot 2\text{HCN}]^{2+}$, of the limiting dissociative mechanism, again in line with the expected trend for such a mechanism.

Table 1. Selected structural parameters for HCN exchange on $[\text{Zn}(\text{HCN})_6 \cdot \text{HCN}]^{2+}$.

$r_1(\text{Zn-N}) / \text{\AA}$	$r_2(\text{Zn}\cdots\text{N}) / \text{\AA}$	$r(\text{N}\cdots\text{HCN-Zn}),$ $/ \text{\AA}$	$\sum r_3 = \sum r_1 + \sum r_2 / \text{\AA}$	$\Delta \sum (\sum r_3^{\ddagger} - \sum r_3^*) / \text{\AA}$
First coordination sphere	Second coordination sphere			
$[\text{Zn}(\text{HCN})_6]^{2+} \cdot \text{HCN}, (C_4)$				
2.20, 2.20, 2.20, 2.20, 2.20, 2.12	6.26	1.90	19.38*	---
$[\text{Zn}(\text{HCN})_5 \cdot 2\text{HCN}]^{2+\ddagger}, (C_1)$				
2.03, 2.21, 2.09, 2.05, 2.21	4.04, 6.14	1.86, 3.62	20.79	+1.41
$[\text{Zn}(\text{HCN})_5 \cdot 2\text{HCN}]^{2+}, (C_1)$				
2.03, 2.03, 2.08, 2.22, 2.22	6.14, 6.14	1.85, 1.85	22.86	---
$[\text{Zn}(\text{HCN})_7]^{2+\ddagger}, (C_2)$				
2.41, 2.39, 2.37, 2.39, 2.09, 2.09, 2.41		---	16.15	-3.38

The overall mechanistic findings demonstrate that as in the case of Li^+ , [17,18] Be^{2+} , [19] and Al^{3+} , [20,21] water and HCN exhibit the same type of exchange mechanism such that HCN can be considered to be a water like solvent.

Besides using HCN as a water-like solvent for quantum chemical studies, hydrogen cyanide is employed as a simplified working model for acetonitrile. To the best of our knowledge there is no $[\text{Zn}(\text{HCN})_6]^{2+}$ structure investigated by x-ray analysis up to know, and we therefore decided to compare the calculated structure of $[\text{Zn}(\text{HCN})_6]^{2+}$ with that of $[\text{Zn}(\text{CH}_3\text{CN})_6]^{2+}$ [2] and $[\text{Zn}(\text{PhCN})_6]^{2+}$ [2] as well as $[\text{Zn}(\text{NC-CN})_6]^{2+}$ [28]. As

expected we find satisfactory agreement between the experimental determined and calculated structures (Table 2).

Table 2. Comparison of measured and calculated (B3LYP/6-311+G**) Zn...NCH bond lengths.

Complex	r(Zn-N) /Å (x-ray)	r(Zn-N) /Å (DFT)	Point group
[Zn(HCN) ₆] ²⁺	-	2.19	<i>O_h</i>
[Zn(CH ₃ CN) ₆] ²⁺	2.134 [2]	2.18	<i>C₁</i>
[Zn(PhCN) ₆] ²⁺	2.108 – 2.157 [2]	2.18	<i>T_h</i>
[Zn(NC-CN) ₆] ²⁺	2.134 [28]	2.19	<i>O_h</i>

DFT: B3LYP/6-311+G**

During the investigation of [Al(HCN)₆·(HCN)]³⁺, we found that the length of the hydrogen bond between HCN in the first and second coordination spheres depends mainly on the charge of the central metal ion. A comparison between [Be(HCN)₄·(HCN)]²⁺ and [Zn(HCN)₆·(HCN)]²⁺ nicely shows that the HCN...HCN hydrogen bond lengths are in the expected range between 1.7 and 1.9 Å (see Figure 5). The slight elongation is understandable since the Zn²⁺ cation is six-coordinate and can compensate the positive charge better than the four-coordinate Be²⁺ cation.

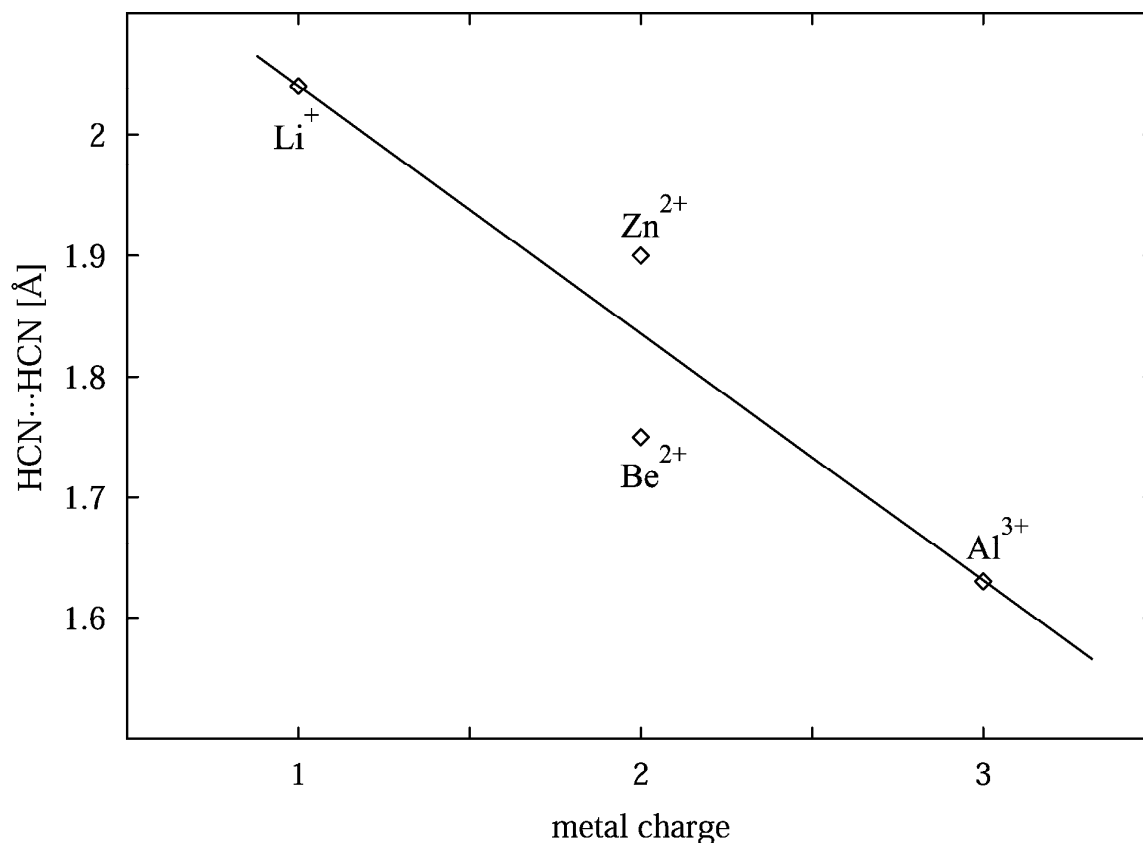


Figure 5. Plot of calculated hydrogen bond lengths for $r(\text{HCN}\cdots\text{NCH})$ in $[\text{M}(\text{HCN})_m \cdot (\text{HCN})]^{n+}$, $\text{M} = \text{Li}$ ($m = 4$, $n = 1$), [22] Be ($m = 4$, $n = 2$), [23a] Zn ($m = 6$, $n = 2$) and Al ($m = 6$, $n = 3$) [21] complexes versus the charge on the metal ion.

A comparison of the dissociative HCN exchange on $[\text{Zn}(\text{HCN})_6]^{2+}$ and $[\text{Al}(\text{HCN})_6]^{3+}$ [21] shows that the sum of the metal-nitrogen bond lengths ($\sum(\text{M-NCH})$) as a quantum chemical descriptor for ΔV^\ddagger is shorter in the case of $\text{M} = \text{Al}^{3+}$ since the attraction depends on the charge of the metal ion. The activation barriers for $[\text{Zn}(\text{HCN})_6]^{2+}$ and $[\text{Al}(\text{HCN})_6]^{3+}$ [21] were found to be 7 and 23.4 kcal mol⁻¹, respectively, and the intermediate in the case of Zn^{2+} is at zero energy relative to the reactant state, but at 12.1 kcal mol⁻¹ for $[\text{Al}(\text{HCN})_6]^{3+}$ [21]. The activation barriers show that the larger zinc ion ($r = 0.74$ Å) has a better ability to form the six-coordinate structure than the much smaller Al^{3+} . The significantly smaller activation barrier for $[\text{Zn}(\text{HCN})_6]^{2+}$ can easily be attributed to the lower charge as compared to $[\text{Al}(\text{HCN})_6]^{3+}$.

Conclusion

The computed structural parameters and activation energies for hydrogen cyanide exchange on $[\text{Zn}(\text{HCN})_6]^{2+}$ show that the limiting dissociative (D) pathway is more favorable than the alternative associative interchange (I_a) mechanism. A comparison of the transition state for the limiting D and associative interchange (I_a) mechanisms, favors the dissociative transition state by $8.9 \text{ kcal mol}^{-1}$. This study clearly outlines how important the consideration of transition states and intermediates in mechanistic studies are.

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