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HCN exchange on $[\text{Cu}(\text{HCN})_4]^+$: a quantum chemical investigation

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HCN exchange on $[\text{Cu}(\text{HCN})_4]^+$: a quantum chemical investigation

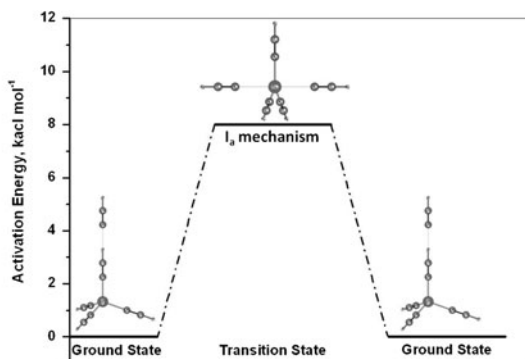
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Computed structural and energetic data indicate an associative interchange (I_a) mechanism for HCN exchange on $[\text{Cu}(\text{HCN})_4]^+$.

Density functional (B3LYP, B3PW91, X3LYP, BP86, PBEPBE, PW91PW91, and M06) and *ab initio* (MP2, MP4sdq, CCSD, and CCSD(T)) calculations with extended basis sets (6-311+G**, TZVP, LANL2DZ+p, and SDD+p, the latter including extra polarization and diffuse functions) indicate that HCN exchange on $[\text{Cu}(\text{HCN})_4]^+$ proceeds via an associative interchange (I_a) mechanism and a D_{3h} transition structure $\{[\text{Cu}(\text{HCN})_5]^+\}^\ddagger$. The activation barrier, relative to the model complex $[\text{Cu}(\text{HCN})_4]^+\cdot\text{HCN}$, varies modestly, depending on the computational level. Typical values are 8.0 kcal M^{-1} (B3LYP/6-311+G**), 6.0 kcal M^{-1} (M06/6-311+G**), and 4.8 kcal M^{-1} (CCSD(T)/6-311+G**//MP2(full)/6-311+G**). Inclusion of an implicit solvent model (B3LYP(CPCM)/6-311+G**) leads to an activation barrier of $5.8 \text{ kcal mol}^{-1}$. Comparison of the HCN exchange mechanisms on $[\text{Li}(\text{HCN})_4]^+$ (limiting associative, A) and $[\text{Cu}(\text{HCN})_4]^+$ (associative interchange, I_a) reveals that π back donation in the equatorial Cu–N bonds in the transition state determines the mechanism.

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In memoriam Prof. Dr Wolf Broda (31.12.1917–4.6.2014).

Keywords: Copper(I); Hydrogen cyanide; Solvent exchange; Mechanism; DFT

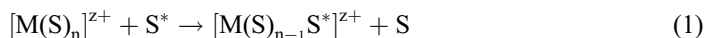
Introduction

Copper ions are one of the so-called micro-nutrients [1] and play an important role as cofactor for cellular enzymes [2], including superoxide dismutase [3] and cytochrome c oxidase [4]. The coordination chemistry of copper ions with proteins is very interesting, because it can coordinate to nitrogen and sulfur donors to form a unique valence state described as Cu(I/II) [5]. The conversion of copper between the oxidized Cu^{2+} and reduced Cu^+ state in biological systems makes copper an important catalytic co-factor for various metabolic reactions [6]. Cu(I) prefers coordination with sulfur donor ligands such as cysteine or methionine, whereas Cu(II) shows some preference for nitrogen donor ligands such as histidine or oxygen donor ligands such as in glutamate or aspartate [7]. However, while the presence of copper ions thus is essential for organisms, free copper ions generally are toxic [8].

In addition to the bioinorganic relevance of copper ions, they are of great interest for catalysis in all oxidation states [9], starting from zero as in the famous Ullmann reaction [10]. In the context of the expected shortage of some precious metals in future, copper can be of great importance [11]. For example, Cu(I) ions have a wide range of catalytic applications, like in azide-alkyne cycloaddition [12], cyclopropanation [13], catalyzed asymmetric allylation of ketones, and ketimines [14], or functionalization of carbonyls, alkenes, and alkynes with N-heterocyclic carbene complexes of copper [15].

In all the aforementioned reactions, ligand exchange is a fundamental process. We can distinguish three main mechanistic pathways: (i) a dissociative (D) process with an intermediate of lower coordination number, where a ligand leaves the first coordination sphere (i.e. a bond is broken) before a new ligand enters; (ii) an associative (A) process with an intermediate of higher coordination number, where the new ligand enters from the second into the first coordination sphere (i.e. a bond is formed) before another ligand leaves the first coordination sphere; and (iii) an interchange (I) process, in which no intermediates of lower or higher coordination number are involved and simultaneous bond formation and bond breakage occurs. Depending on the degree of bonding between the ligands involved in the exchange, interchange reactions can be more dissociative (I_d) or more associative (I_a) in nature [16]. Experimentally, the activation volume (ΔV^\ddagger) can be used to distinguish between the different ligand exchange mechanisms [17, 18].

Solvent exchange represents a special case of ligand exchange. They involve the displacement of a solvent molecule in the first coordination sphere by another solvent molecule from the second coordination sphere, as shown in equation (1). The study of this type of reactions, both experimentally and computationally, provides valuable insights and understanding of the reactivity of metal ions in chemical and biological systems, such as carbonic anhydrase, carboxypeptidase A, thermolysin, and alcohol dehydrogenase [19].



Hydrogen cyanide is a well-known water-like solvent [20]. While the high toxicity severely limits its application in experimental organic and inorganic chemistry, HCN serves as a good model for CH_3CN in quantum chemical studies [21]. Our DFT (B3LYP/6-311+G**) calculations on HCN exchange mechanisms revealed a limiting associative (A) mechanism for $[\text{Li}(\text{HCN})_4]^+$, as a model for $[\text{Li}(\text{CH}_3\text{CN})_4]^+$ [21], and an associative

interchange (I_a) mechanism for $[\text{Be}(\text{HCN})_4]^{2+}$ [22]. In the case of $[\text{Zn}(\text{HCN})_6]^{2+}$ [23] and $[\text{Al}(\text{HCN})_6]^{3+}$ [24], several mechanisms are possible, but the limiting dissociative (D) pathway is more favorable than alternative mechanisms. Interestingly, the same mechanistic preferences were computed for water exchange: limiting associative for $[\text{Li}(\text{H}_2\text{O})_4]^+$ [25], associative interchange for $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ [26], and limiting dissociative both for $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ [27], and for $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ [28].

In this study, we investigate the mechanism of HCN exchange on $[\text{Cu}(\text{HCN})_4]^+$. In addition, we evaluate the performance of several popular density functionals and commonly used basis sets.

Quantum chemical methods

All structures were fully optimized with no constraints other than symmetry, where applicable, and characterized by computation of vibrational frequencies as local minima or transition states. Relative energies were corrected for zero point energies. We applied the density functionals BP86 [29, 30], B3LYP [31–33], B3PW91 [31, 34], X3LYP [35], PBEPBE [36], PW91PW91 [34], M06 [37], and compared these to MP2 [38, 39] and CCSD(T) [40]. The frozen core approximation was used unless stated otherwise. We used the basis sets 6-311+G** [39], TZVP [41], LANL2DZ [42], and SDD [43]. We added polarization functions [44] and diffuse functions [45] to LANL2DZ and SDD; the resulting basis sets are denoted as LANL2DZ+p and SDD+p, respectively. The influence of the bulk solvent was probed using the CPCM model [46] for B3LYP/6-311+G**. Corrections for BSSE, computed using the counterpoise method [47] at B3LYP/6-311+G**, were found to be negligible. The Gaussian 09 suite of programs was used throughout [48].

Results and discussion

X-ray structures reveal Cu–N bond lengths between 1.98 and 2.02 Å for $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ [49, 50, 51] while values between 1.97 and 2.03 Å are found for $[\text{Cu}(\text{PhCN})_4]^+$ [52, 53]. Our calculated bond lengths in $[\text{Cu}(\text{HCN})_4]^+$ are in good agreement with these values: depending on the theoretical level, we obtain Cu–N distances of 1.96–2.05 Å (table 1).

The established way to model the second coordination sphere is by adding one or two additional ligand molecules that are not bound directly to the metal ion, but by, e.g. hydrogen bonds, to the ligands of the first coordination sphere [26, 27, 54]. The resulting complex $[\text{Cu}(\text{HCN})_4]^+\cdot\text{HCN}$, of C_{3v} symmetry (figure 1), is taken as the reactant in the solvent exchange reaction. The N···H distance, i.e. the hydrogen bond length, is about 2 Å (table 1). The additional HCN molecule is bound to $[\text{Cu}(\text{HCN})_4]^+$ by 9–10 kcal M^{-1} , depending on the method. Interestingly, the same binding energy was computed for an HCN molecule bound to $[\text{Li}(\text{HCN})_4]^+$ [21].

The B3LYP/6-311+G** interaction energy for the linear HCN dimer is 3.5 kcal M^{-1} . The binding energy in $[\text{Cu}(\text{HCN})_4]^+\cdot\text{HCN}$ may seem high in comparison, but a significant part is due to electrostatic (ion – induced dipole) interaction. This is typical for gas-phase calculations, in which stabilization of ions by the medium is absent. Modeling the influence of the bulk solvent using the CPCM formalism [46] reduces the binding energy to 2.3 kcal M^{-1} .

Table 1. Selected structural parameters for HCN exchange on $[\text{Cu}(\text{HCN})_4]^+\cdot\text{HCN}$ calculated with different methods and basis sets.

Method	$[\text{Cu}(\text{HCN})_4]^+$		Ground state $[\text{Cu}(\text{HCN})_4]^+\cdot\text{HCN}$				Transition state $\{[\text{Cu}(\text{HCN})_5]^+\}^\ddagger$			
	Cu–NCH Å	N \cdots H Å	$r_1(\text{Cu–N})$ Å	$r_1(\text{Cu}\cdots\text{N})$ Å	$\sum r_1$ Å	$r_2(\text{Cu–N})$ Å	$r_2(\text{Cu}\cdots\text{N})$ Å	$\sum r_2$ Å	$\Delta\sum = \sum r_2 - \sum r_1$ Å	
B3LYP/6–311+G**	2.03	2.04	2.02, 2.04	6.28	14.42	1.99	2.68	11.33	–3.09	
B3LYP/TZVP	2.03	2.03	2.04, 2.04	6.28	14.44	2.00	2.63	11.26	–3.18	
B3LYP/ LANL2DZ+p	2.05	1.97	2.03, 2.06	6.25	14.47	2.06	2.38	10.94	–3.53	
B3LYP/SDD+p	2.01	1.97	1.99, 2.01	6.21	14.23	1.97	2.53	10.97	–3.26	
B3PW91/6–311+G**	2.01	2.02	2.00, 2.01	6.25	14.28	1.97	2.64	11.19	–3.09	
X3LYP/6–311+G**	2.03	2.03	2.02, 2.04	6.27	14.41	1.99	2.65	11.27	–3.14	
BP86/6–311+G**	1.98	1.99	1.98, 1.98	6.22	14.14	1.94	2.59	11.00	–3.14	
PBEPBE/6–311+G**	1.98	1.99	1.97, 1.98	6.22	14.13	1.94	2.59	11.00	–3.13	
PW91PW91/ 6–311+G**	1.98	1.98	1.97, 1.98	6.20	14.11	1.94	2.56	10.94	–3.17	
M06/6–311+G**	2.02	1.99	2.00, 2.02	6.23	14.29	1.99	2.50	10.97	–3.32	
M06/LANL2DZ+p	2.03	1.93	2.01, 2.03	6.20	14.30	2.04	2.36	10.84	–3.46	
M06/SDD+p	2.00	1.93	1.98, 2.00	6.17	14.15	1.97	2.47	10.85	–3.30	
MP2(full)/ 6–311+G**	1.96	2.06	1.95, 1.96	6.27	14.10	1.93	2.58	10.95	–3.15	
MP2(full)/TZVP	2.01	2.07	1.98, 2.01	6.31	14.32	1.97	2.60	11.11	–3.21	
B3LYP(CPCM)/ 6–311+G**	2.03	2.07	2.02, 2.03	6.32	14.43	1.98	2.75	11.44	–2.99	

The reaction pathway for the HCN exchange involves the movement of the HCN moiety that comprises the modeled second coordination sphere toward one of the faces of the $[\text{Cu}(\text{HCN})_4]^+$ tetrahedron. The N \cdots H bond is broken and a new Cu \cdots N contact is realized. In the resulting transition structure $\{[\text{Cu}(\text{HCN})_5]^+\}^\ddagger$, a trigonal bipyramid of D_{3h} geometry (figure 2), the equatorial Cu–N bonds are shortened by 0.03 Å, whereas the incoming and leaving HCN ligands have Cu \cdots N distances of around 2.6 Å (table 1).

These structural changes suggest an associative interchange (I_a) mechanism. This is corroborated by the change in the sum of the metal ligand distances upon going from the reactant state to the transition state ($\Delta\sum$), which provides a good descriptor of the nature of the mechanism. The sign of this value generally agrees well with the sign of the experimental value of the activation volume (ΔV^\ddagger) [55, 56]. The calculated $\Delta\sum$ values are negative (–3.0 to –3.5 Å, see table 1) for all levels employed, thus confirming the classification of the mechanism as associative interchange (I_a).

The ionic radii of Cu(I) (0.60 Å) and Li(I) (0.59 Å) are approximately the same [57], therefore a comparison between the two exchange reactions with different mechanisms is rather instructive. The Cu–N bonds in the reactant complex $[\text{Cu}(\text{HCN})_4]^+\cdot\text{HCN}$ are 0.03 Å shorter than the Li–N bonds in $[\text{Li}(\text{HCN})_4]^+\cdot\text{HCN}$ (B3LYP/6-311+G**) [21]. This can be

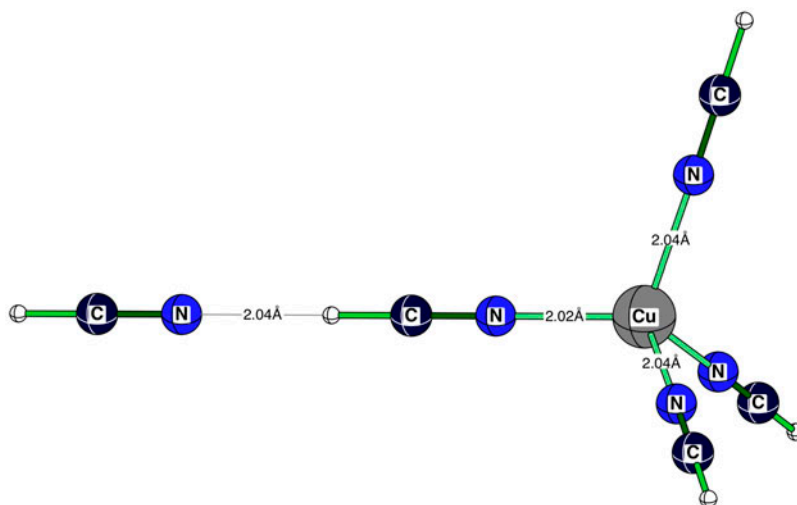


Figure 1. Calculated structure (B3LYP/6-311+G**) of the reactant state $[\text{Cu}(\text{HCN})_4]^+ \cdot \text{HCN}$.

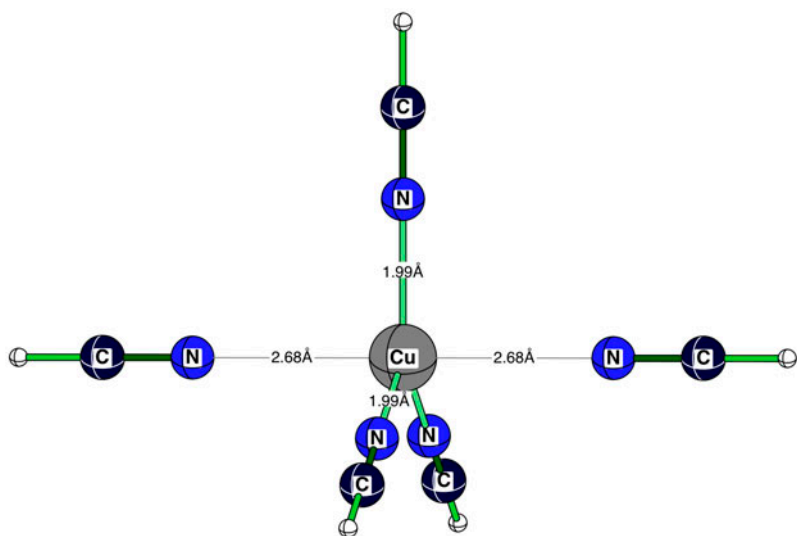


Figure 2. Calculated structure (B3LYP/6-311+G**) of the transition state $\{[\text{Cu}(\text{HCN})_5]^+\}^\ddagger$.

attributed to the overlap of filled copper d orbitals with π^* orbitals of the HCN ligands (π back donation) [58, 59].

The metal ligand interactions in the D_{3h} intermediate $[\text{Li}(\text{HCN})_5]^+$ are essentially electrostatic and the equatorial bonds (2.13 Å) and the axial bonds (2.25 Å) are of comparable length. This contrasts sharply with the transition state $\{[\text{Cu}(\text{HCN})_5]^+\}^\ddagger$, which has long (2.68 Å), weak axial bonds and strong equatorial Cu–N bonds that are even shorter (1.99 Å) than in the ground state [60]. The reason for this is that π back donation contributes significantly to the equatorial bonds. In a hypothetical intermediate, the equatorial bonds would

be longer (like in $[\text{Li}(\text{HCN})_5]^+$) and π back donation would be diminished, which would lead to a destabilization.

Ligand exchange in $[\text{Be}(\text{HCN})_4]^{2+}\cdot\text{HCN}$ also proceeds through an associative interchange mechanism, despite largely electrostatic metal ligand interactions [22]. Here, all Be–N distances are short, due to the higher charge of Be^{2+} and its smaller ion radius (0.27 Å) [57], and steric repulsion between the ligands prohibits a stable pentacoordinate intermediate.

As noted previously [23], the length and strength of the $\text{HCN}\cdots\text{HCN}$ hydrogen bonds between first and second coordination spheres correlate with the charge on the central metal ion. The values for $[\text{Cu}(\text{HCN})_4]^+\cdot\text{HCN}$ (2.04 Å) and for the HCN-dimer (2.23 Å) fit well in this trend (figure 3).

The energy profile, computed at B3LYP/6-311+G**, of the ligand exchange reaction in $[\text{Cu}(\text{HCN})_4]^+\cdot\text{HCN}$ is depicted in scheme 1. For comparison, we include the profile for $[\text{Li}(\text{HCN})_4]^+\cdot\text{HCN}$ [21]. The calculated activation barrier for Cu^+ , 8.0 kcal M^{-1} , is higher than for Li^+ (5.5 kcal M^{-1}); we tentatively ascribe this difference to the higher strength of the Cu–N bonds due to π back bonding (*vide supra*).

It is instructive to compare the performance of different density functionals, *ab initio* methods, and basis sets, in particular when transition metal complexes are involved [see, e.g. 61]. Structural parameters computed at the levels employed in this study are given in table 1, while the calculated relative energies are summarized in table 2.

The influence of methods and basis sets on the structures turns out to be small. In particular, the same mechanistic conclusion is reached for all computational levels, as can be seen clearly from the $\Delta\Sigma$ values. In all cases, a C_{3V} structure is computed for $[\text{Cu}(\text{HCN})_4]^+\cdot\text{HCN}$, whereas the transition state $\{[\text{Cu}(\text{HCN})_5]^+\}^\ddagger$ has D_{3h} symmetry. The activation barriers show a bit more variation, but here, too, the same conclusion with respect to the mechanism is reached for all levels.

The MP2 method is well known for its tendency to underestimate activation barriers [39]. We noted this in previous work [62] and indeed, the barriers computed at MP2 are lower than the values calculated using commonly employed density functional methods.

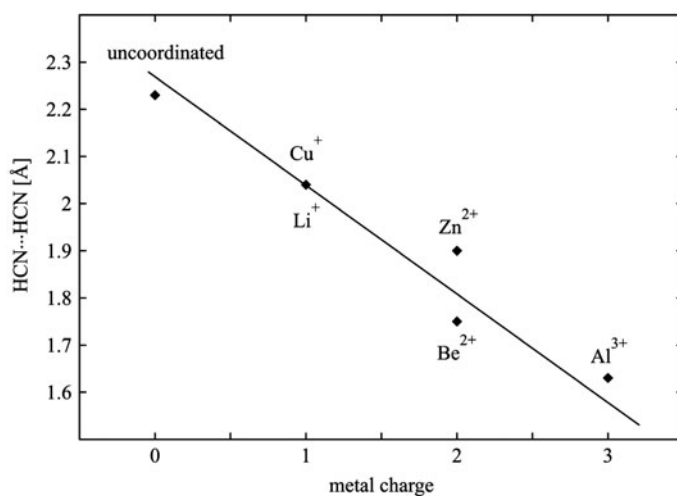
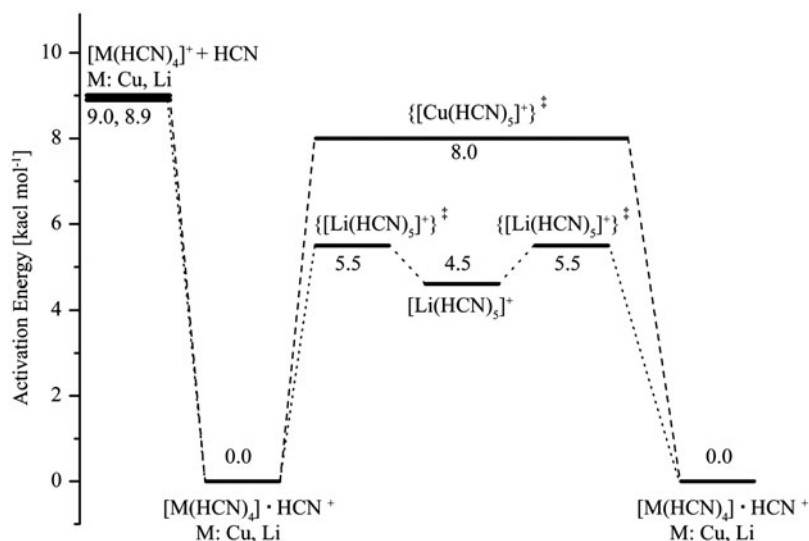


Figure 3. Calculated (B3LYP/6-311+G**) HCN \cdots HCN hydrogen bond lengths in free HCN dimer and in $[\text{M}(\text{HCN})_m]^{n+}\cdot\text{HCN}$ vs. the charge on the metal ion.



Scheme 1. Calculated (B3LYP/6-311+G**) energy profile for the HCN exchange pathway on the complexes $[\text{Cu}(\text{HCN})_4]^+\cdot\text{HCN}$ and $[\text{Li}(\text{HCN})_4]^+\cdot\text{HCN}$ [21].

Table 2. Calculated relative energies for HCN exchange in $[\text{Cu}(\text{HCN})_4]^+\cdot\text{HCN}$ using different methods and basis sets.

Method	Binding of HCN to $[\text{Cu}(\text{HCN})_4]^+$ kcal M^{-1}	Activation energy, kcal M^{-1}
B3LYP/6-311+G**	9.0	8.0
B3LYP/TZVP	9.0	7.9
B3LYP/LANL2DZ+p	9.6	7.3
B3LYP/SDD+p	9.5	7.5
B3PW91/6-311+G**	8.8	8.6
X3LYP/6-311+G**	9.4	7.9
BP86/6-311+G**	8.7	9.4
PBEPBE/6-311+G**	9.5	8.7
PW91PW91/6-311+G**	9.8	8.8
M06/6-311+G**	10.4	6.0
M06/6-311+G**//B3LYP/6-311+G**	10.0	6.6
M06/LANL2DZ+p	11.2	6.0
M06/SDD+p	10.8	6.1
MP2(full)/6-311+G**	9.2	5.6
MP2(full)/TZVP	9.2	5.4
MP2/6-311+G**//B3LYP/6-311+G**	9.2	5.9
MP2(full)/6-311+G**//B3LYP/6-311+G**	9.3	5.9
MP4SDQ/6-311+G**//B3LYP/6-311+G**	9.0	7.5
CCSD/6-311+G**//B3LYP/6-311+G**	8.8	5.2
CCSD(T)/6-311+G**//B3LYP/6-311+G**	9.0	5.5
MP4SDQ/6-311+G**//MP2(full)/6-311+G**	9.0	8.4
CCSD/6-311+G**//MP2(full)/6-311+G**	8.7	4.4
CCSD(T)/6-311+G**//MP2(full)/6-311+G**	8.9	4.8
B3LYP(CPCM)/6-311+G**	2.3	5.8

However, barriers computed using high-level *ab initio* methods, CCSD and CCSD(T), using the structures optimized at B3LYP/6-311+G** and at MP2(full)/6-311+G**, are even lower. Therefore, we consider the MP2 barriers to be reliable.

The more recent M06 density functional [37] also consistently yield lower activation barriers, close to the MP2 and CCSD(T) values. This functional is recommended by the authors as a good, versatile functional for main group and transition metal chemistry and our results appear to confirm this. Unfortunately, we encountered severe difficulties during the structure optimizations of the hydrogen bonded complex $[\text{Cu}(\text{HCN})_4]^+\cdot\text{HCN}$ using this functional.

The D_{3h} transition state can be viewed as $\{\text{HCN}\cdots[\text{Cu}(\text{HCN})_3]^+\cdots\text{NCH}\}^\ddagger$, i.e. as $[\text{Cu}(\text{HCN})_3]^+$ with two weakly bound HCN molecules. When the bulk solvent is modeled by means of the CPCM method [46], the axial bonds are elongated and the activation barrier is reduced, indicating additional stabilization of the $[\text{Cu}(\text{HCN})_3]^+$ moiety by the medium. The changes are comparatively minor, however, and the characteristics of the mechanism remain unchanged.

Conclusion

According to our density functional and *ab initio* calculations, exchange of HCN on $[\text{Cu}(\text{HCN})_4]^+$ proceeds via an associative interchange (I_a) mechanism. Starting from the model complex $[\text{Cu}(\text{HCN})_4]^+\cdot\text{HCN}$, we compute activation barriers between 5 and 9 kcal M^{-1} , depending on the method. The trigonal bipyramidal transition state has D_{3h} symmetry, in which the $[\text{Cu}(\text{HCN})_3]^+$ moiety is stabilized by π back donation.

Practical note

Our work shows that both the popular B3LYP functional [33] and the modern M06 functional [37] appear well suited for the investigation of ligand exchange reactions on transition metal ions. When possible, high-level *ab initio* calculations are recommended as benchmark. Extended basis sets, including diffuse and polarization functions, are required to avoid basis set superposition error. We advise against the use of Hartree-Fock for preliminary calculations, as these fail to reproduce the characteristics of the potential energy surface.

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