

Computational evaluation of unsaturated carbonitriles as neutral receptor model for beryllium(II) recognition

Ahmad Nazmi Rosli · Mohd Rais Ahmad ·
Yatimah Alias · Sharifuddin Md Zain ·
Vannajan Sanghiran Lee · Pei Meng Woi

Received: 26 September 2014 / Accepted: 13 November 2014 / Published online: 30 November 2014
© Springer-Verlag Berlin Heidelberg 2014

Abstract Design of neutral receptor molecules (ionophores) for beryllium(II) using unsaturated carbonitrile models has been carried out via density functional theory, G3, and G4 calculations. The first part of this work focuses on gas phase binding energies between beryllium(II) and 2-cyano butadiene (2-CN BD), 3-cyano propene (3-CN P), and simpler models with two separate fragments; acrylonitrile and ethylene. Interactions between beryllium(II) and cyano nitrogen and terminal olefin in the models have been examined in terms of geometrical changes, distribution of charge over the entire π -system, and rehybridization of vinyl carbon orbitals. NMR shieldings and vibrational frequencies probed charge centers and strength of interactions. The six-membered cyclic complexes have planar structures with the rehybridized carbon slightly out of plane (16° in 2-CN BD). G3 results show that in 2-CN BD complex participation of vinyl carbon further

stabilizes the cyclic adduct by $16.3 \text{ kcal mol}^{-1}$, whereas, in simpler models, interaction between beryllium(II) and acetonitrile is favorable by $46.4 \text{ kcal mol}^{-1}$ compared with that of ethylene. The terminal vinyl carbon in 2-CN BD rehybridizes to sp^3 with an increase of 7 % of s character to allow interaction with beryllium(II). G4 calculations show that the Be(II) and 2-CN BD complex is more strongly bound than those with Mg(II) and Ca(II) by 98.5 and $139.2 \text{ kcal mol}^{-1}$, respectively. QST2 method shows that the cyclic and acyclic forms of Be(II)-2-CN BD complexes are separated by $12.3 \text{ kcal mol}^{-1}$ barrier height. Overlap population analysis reveals that Ca(II) can be discriminated based on its tendency to form ionic interaction with the receptor models.

Keywords Beryllium · Density functional theory · G3 · G4 · Ionophore

Electronic supplementary material The online version of this article (doi:10.1007/s00894-014-2533-9) contains supplementary material, which is available to authorized users.

A. N. Rosli · Y. Alias · S. M. Zain · V. S. Lee · P. M. Woi (✉)
Department of Chemistry, Faculty of Science Building,
University of Malaya, Kuala Lumpur 50603, Malaysia
e-mail: pmwoi@um.edu.my

A. N. Rosli
e-mail: nazmi86@siswa.um.edu.my

Y. Alias
e-mail: yatimah70@um.edu.my

S. M. Zain
e-mail: smzain@um.edu.my

V. S. Lee
e-mail: vannajan@gmail.com

M. R. Ahmad
Smart Sensor Solutions, No. 24, Jalan BK9/5F, Bandar
Kinrara 47180, Puchong, Selangor, Malaysia
e-mail: mohdrais.ahmad@gmail.com

Introduction

The chemistry of beryllium compounds can be explained in terms of charge to radius ratio, electronegativity and electron deficiency of beryllium atom and its charged species. In keeping with these reasoning the structure and reactivity of beryllium (I and II) compounds closely resembles those of aluminum and boron, and atypical to its group II neighbors [1]. Due to its light, stiff, and stable structure, beryllium has increasingly been employed in industrial applications, especially in its beryllium-copper alloy forms [2–4]. Furthermore, the electron deficient nature of divalent beryllium compounds can be exploited as catalyst in polymerization process and synthesis [4–6]. However, beryllium and its compounds are Category 1 carcinogens. Direct exposure to elemental beryllium has been considered as potential health hazard and several reports on chronic medical conditions due to beryllium had been documented [7]. Schleyer, Schaefer and their co-workers

have demonstrated earlier the use of computational methods in estimating stabilities of organometallic systems involving beryllium [8–10]. Recently Clark, Frenking and their co-workers have exploited advanced *ab initio* and DFT methods in investigating beryllium-ligand interaction [11, 12]. DFT [13, 14] method has widely been utilized in obtaining reliable molecular geometries and properties. G3 [15] composite method on the other hand is more useful in producing accurate energetics data; within the types of molecules covered in its test sets, the Gn methods have been demonstrated to be able to reproduce experimental results.

We adopt computational methods in order to gain insights on the interaction of doubly charged beryllium cation (Be(II)) with unsaturated carbonitriles in our attempt to design neutral receptor molecule or ionophore for beryllium(II). In the first part of this work we focus on 2-cyanobutadiene (2-CN BD) and 3 cyanopropene (3-CN P) to represent unsaturated carbonitriles (Fig. 1). Eventually, this investigation is desired to reveal to us viable options of beryllium ionophore having high selectivity toward beryllium — against magnesium(II), calcium(II), and aluminum(III).

Structure 1 is employed in order to evaluate the binding of beryllium(II) with lone electron pair in the cyano group, direct participation of a carbon-carbon double bond in cation-receptor interaction and stabilization of the Be(II) -receptor complex due to π -conjugation. A carbonitrile receptor model that lacks conjugation, i.e., structure 2 elucidates the participation of carbonitrile and olefin moieties but without π -system. Simpler models have been evaluated for comparison — these are small molecule fragments of structures 1 and 2 (ethylene, acetonitrile, and acrylonitrile) that give useful information with much less computation time. It is insightful to confirm that metal cations could actually form strong interaction with vinyl moieties, and this finding could extend the applications of beryllium in chemical sensor, preparative procedure and polymerization.

We have reported earlier the interactions of unsaturated carbonitriles with metal cations [16, 17]. We have highlighted that in the absence of conjugation, the imparted positive charge from the cation is mainly transferred to the α -protons and the cyano bond remains intact. On the contrary, in conjugated carbonitriles such as acrylonitrile, the transferred positive charge is distributed over the entire π -network and the

cyano bond broken to afford a ketenimine structure [18]. During the preparation of this report we have also investigated the possibility of employing carbonitrile-carboxaldehyde receptors as selective recognition molecules for group II divalent cations. We have proposed that electron sharing versus ionic type interaction could elucidate the nature of heteroatom-metal binding and provide rationale in discrimination of group I cations and explanation in the experimentally determined selectivity.

Results and discussion

Optimized geometries

The interaction of beryllium(II) species with 2-cyanobutadiene (1) presumably is initiated by sharing of cyano nitrogen lone electron pair to beryllium(II) empty orbital. In the acyclic complex the immediate product is destabilizing due to repulsion between positively charged neighboring nitrogen and beryllium cation. Stabilization can be achieved if the positive charge on nitrogen is distributed over the entire π -network. Results in Table 1 show that beryllium(II) has donated 52 % of its charge (reduced to 0.963) to structure 1 in the acyclic complex. Beryllium(II) imparts further its positive charge to the diene moiety by interacting with C4 resulting in only 23 % of its positive charge (reduced to 0.454) remains on beryllium. Distribution of positive charge over the π -network in the acyclic complex moves positive center further from beryllium atom, and results in 4 % shortening of the C2-C5 bond and 2 to 3 % elongation of C5-N6 (the cyano bond) and C1-C2 bonds (Figs. 2 and 3). This result indicates that as we have observed earlier in acrylonitrile-metal complexes, the cyano bond in 1-Be is broken and a bent ketenimine moiety is formed. There is no significant change in the C3-C4 bond other than the out-of-plane (57.8° C1-C2-C3-C4 dihedral angle) twist of the olefin moiety. The C3-C4 bond is elongated by about 6 % due to the interaction of beryllium(II) with the π -bond orbitals on C3-C4 for the formation of Be-C4 bond. The 2-cyanobutadiene-metal interaction is the strongest in cyclic 1-Be compared to those with magnesium(II) and calcium(II), inspected based on the structural changes to the receptor induced by the interactions with divalent cations. Beryllium pulls the terminal vinyl atom and the cyano nitrogen atom closer together at 2.89 \AA making a 117.0° N6-Be-C4 angle. Likewise, the metal-C4, the metal-N6 bonds, and the C4-N6 distance are the shortest with beryllium(II). The Ca-C4 and the Mg-C4 (2.30 \AA) bond distances are 65 and 29 % longer, respectively, compared to Be-C4. Moreover, the Ca-N6 bond length is 48 % longer than Be-N. Weaker interactions give smaller N6-metal-C4 angles; N6-Ca-C4 and N6-Mg-C4 affords 76° and 35° smaller N6-metal-C4 angle, compared to N6-Be-C4. The C1-C2 only

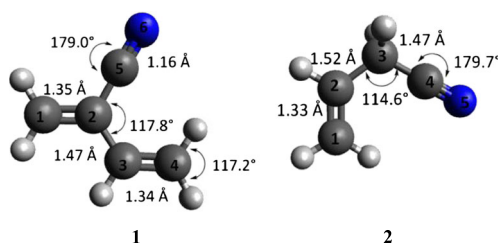


Fig. 1 Computed B3LYP/6-31+G(d,p) geometries of 1(2-CN BD) and 2(3-CN P) color scheme gray C, white H, blue N

Table 1 Mulliken atomic charges for 2-CN BD, 3-CN P, and its complexes with beryllium(II)

	2-CN BD			3-CN P		
	1	Acyclic 1-Be	Cyclic 1-Be	2	Acyclic 2-Be	Cyclic 2-Be
C1	-0.153	-0.032	-0.097	-0.278	-0.176	-0.258
C2	0.753	0.223	0.852	-0.034	-0.029	0.191
C3	-0.138	0.119	0.078	-0.240	-0.189	-0.305
C4	-0.174	-0.229	-0.330	0.221	0.150	0.267
C5	-0.532	-0.154	-0.487	NA	NA	NA
N	-0.514	-0.017	0.150	-0.496	-0.007	0.128
Be	NA	0.963	0.454	NA	1.02	0.466

experiences minor structural changes due to its position being further away from the receptor-metal binding sites, and not significantly affected by the complex π -network.

Mulliken charge analysis indicates that the interaction of beryllium(II) ion with 1 results in reduction of 77.3 % of the positive charge on beryllium (Table 1). The cyano nitrogen experiences the largest increase in positive charge (0.66), followed by C3 with 0.22. This accounts for most of the positive charge donated from beryllium(II) analyte. Due to interaction with Be(II), the cyano carbon (C5) is expected to be more reactive and electrophilic, having a vinyl cation characteristic. Bending of the C2-C5-N6 bond from linearity to allow interaction between Be(II) and C5 is balanced with avoidance of forming C2-C5 allenic double bond and vinyl cation. This balancing act results in almost a full covalent bond between Be(II) and C4 with 1.78 Å bond length, and the biggest accumulation of negative charge on C2 and C4 — the latter is directly favorable to the highly electronegative beryllium atom (Table 1).

The six-membered cyclic 1-Be complex is best viewed as an almost flat structure except for the 16° out of plane involving C5-C2-C3-C4 atoms (Table 2). The carbon and beryllium

centers involved in the new C4-Be bond exhibit significant sp^3 -like character. The p orbital in C4, initially forms π -bond between C3 and C4, rehybridizes to sp^3 hybrid orbital, taking the two π -electrons with it to the beryllium empty orbitals (Fig. 4). This leaves C3 as a positively charged center, sharing the positive charge over the entire π -system. Natural bond orbital (NBO) analysis shows 18 % decrease in s character in the rehybridized p orbital in C4. This is in keeping with the observed decrease in the H10-C4-H11 bond angle from 117° to 111° (Table 3). This explanation is consistent with the observed GIAO NMR shieldings described in the following section.

In the absence of π -conjugation (diene moiety), interaction of beryllium(II) with 3-cyanopropene (receptor model 2) results in longer $C_{\text{vinyl}}\text{-Be}$ (1.82 Å) and only slightly shorter $\text{Be-N}_{\text{cyano}}$ bond (1.60 Å, compared to 1.61 Å in cyclic 1-Be). This is consistent with the above reasoning that weaker interaction (longer $C_{\text{vinyl}}\text{-Be}$ bond) between beryllium and vinyl carbon results from the absence of π -conjugation. Likewise, in the absence of conjugation, the C-C bond adjacent to the cyano group is longer in structure 2 (1.46 Å), as compared to that in structure 1 (1.44 Å). Despite the apparent differences in bond distances, the C-N-Be and C-C-N bond angles in both receptor models are very similar (about 100° and 155°, respectively). As predicted, in the absence of conjugation the remaining positive charge on beryllium is higher in cyclic 2-Be (0.466) compared to that in cyclic 1-Be (0.454). Moreover, the positive charge on carbon atom (C2) adjacent to C-Be bond is higher in cyclic 2-Be (0.191), whereas in cyclic 1-Be, after distributing to three carbon atoms, only 0.078 of Mulliken charge remains on the respective carbon (C3). The cyclic 2-Be

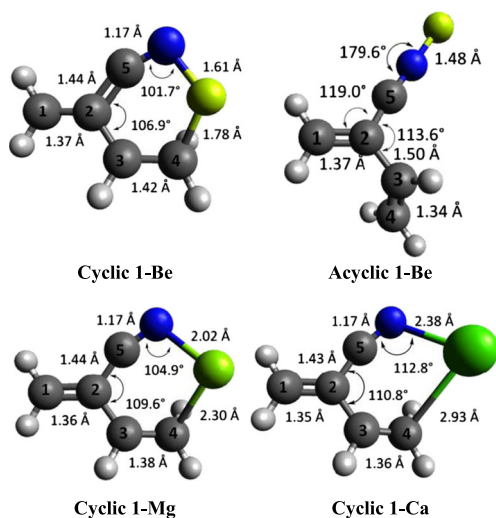
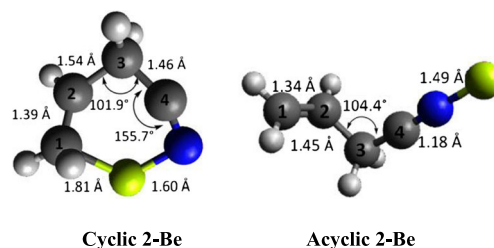
**Fig. 2** Optimized geometries of Be(II)-2-CN BD cyclic complex, Be(II)-2-CN BD acyclic complex, Mg(II)-2 CN BD cyclic complex, and Ca(II)-2 CN BD cyclic complex**Fig. 3** Optimized geometries of Be(II)-3-CN P cyclic complex and Be(II)-3-CN P acyclic complex

Table 2 Dihedral angles of 2-CN BD, 3-CN P, and its complexes with Be(II)

2-CN BD			
Dihedral angles	1 (°)	Cyclic 1-Be (°)	Acyclic 1-Be (°)
C1-C2-C3-C4	180	169.8	58
C2-C4-N-Be	NA	5.7	178.8
C5-C2-C3-C4	0	-16.1	-119.7
N-C5-C1-C2	180	165.6	-179.7
C1-C2-C5-N	180	165.6	178.6
3-CN P			
Dihedral angles	2 (°)	Cyclic 2-Be (°)	Acyclic 2-Be (°)
C1-C2-C3-C4	-0.02	30.5	-99.3
C1-C3-N-Be	NA	11.3	-99.9
C3-C4-N-Be	NA	-5.8	-164.0
C1-C2-N-Be	NA	25.9	-70.4

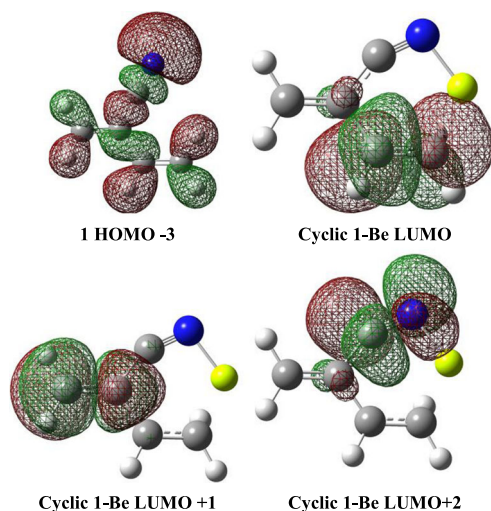
Table 3 Bond angle in 2-CN BD, 3-CN P, and its complexes with Be(II)

2-CN BD			
Bond angles	1 (°)	Cyclic 1-Be (°)	Acyclic 1-Be (°)
C5-N-Be	NA	101.7	179.6
C2-C5-N	179.0	153.4	174.4
H10-C4-H11	117.2	110.8	117.0
C3-C2-C5	117.8	106.9	113.6
C1-C2-C5	119.1	127.0	119.0
3-CN P			
C4-N-Be	NA	100.3	177.5
C3-C4-N	179.9	155.5	175.2
H7-C1-H8	117.2	113.8	116.7
C2-C3-C4	114.6	102.0	104.0
C1-C2-C3	126.2	125.5	122.0

complex also exhibits an almost flat structure with 30° dihedral angle for C1-C2-C3-C4 (Table 2). Meanwhile, the interaction of beryllium(II) with acyclic form of 3-CN P showed similar trend with the acyclic 2-CN BD with only 50 % of Be(II) charge transferred to the unconjugated receptor 2 resulting in 1.02 of Mulliken charge remains on beryllium atom. The acyclic 2-Be complex lacks interaction between C1 vinyl carbon with Be(II). Consequently, the greater extent of positive charge retains by beryllium atom is confirmed by the negligible change in C1 Mulliken charge (in acyclic 2-Be). The C1 of cyclic 2-Be complex had been proposed to undergo rehybridization from sp^2 to sp^3 as indicated by the decrease in the H7-C1-H8 angle from 117.2° to 113.8°.

NMR shifts and vibrational frequencies

Nuclei experiencing deshielding effect due to lack of electron density or localization of positive charge are probed using ^{13}C

**Fig. 4** Frontier orbitals of 1 and its cyclic complex with Be(II)

NMR shifts — increased chemical shifts are predicted for these nuclei. Cyclic 1-Be GIAO studies (Table 4) show that C3 and C1 experience the highest deshielding effects, with 88 % and 57 % increase in carbon chemical shifts, respectively, indicating the largest accumulation of positive charge on these nuclei. Moreover, consistent with the proposed rehybridization of C4 to sp^3 -like, this carbon atom experiences 52 % decrease in chemical shift from 107.8 to 56.3 ppm due to shielding. Likewise, build-up of positive charge increases the chemical shift in C5 by 45 % (from 98.7 to 142.7 ppm) due to deshielding effect. Moreover, the cyclic 2-Be complex also experiences similar deshielding effect due to localization of positive charge only on one carbon nucleus (C2, adjacent to C1-Be), instead of two carbon nuclei observed in cyclic 1-Be, with 74 % (from 135.0 to 235.1 ppm) increase in chemical shift. As predicted, the C1 vinyl carbon in cyclic 2-Be, shows the chemical shift decreases by 60 % (from 124.3 to 73.9 ppm) due to shielding. This observation supports the proposed rehybridization of the C1 vinyl carbon from sp^2 to sp^3 -like to allow covalent type interaction with beryllium. The two complexes, cyclic 1-Be and cyclic 2-Be exhibit a similar trend in nitrogen chemical shifts. The nitrogen nuclei are shielded due to interaction with Be(II), and the cyclic complexes show significantly greater extents of this effect. The absence of π -network in cyclic 2-Be does not influence the shielding on nitrogen nuclei.

Vibrational frequency analysis (Table 5) shows that Be-N bond in the acyclic 1-Be complex stretch at 884.3 cm^{-1} and the Be-N and C5-Be in the cyclic 1-Be complex stretch at 892.5 cm^{-1} and 665.0 cm^{-1} , respectively. These are comparable to the vibrational frequencies obtained at the same level of theory in hydrogen cyanide-Be(II) and ethylene-Be(II) complexes (970.7 cm^{-1} and 721.5 cm^{-1}). The observed frequencies are consistent with the reasoning that lower energies (lower frequencies) are needed to stretch weaker bonds and

Table 4 GIAO ^{13}C NMR shifts (ppm) with TMS reference of 2-CN BD, 3-CN P, and its complexes with Be(II)

	2-CN BD			3-CN P		
	1	Cyclic 1-Be	Acyclic 1-Be	2	Cyclic 2-Be	Acyclic 2-Be
C1	116.3	182.6	182.8	124.3	73.9	146.6
C2	113.1	106.2	93.2	135.0	235.1	98.0
C3	121.1	228.2	103.8	24.3	27.4	15.0
C4	107.8	56.3	143.1	120.2	151.4	154.3
C5	98.7	142.7	149.5	NA	NA	NA
N	272.3	230.3	130.1	297.3	220.3	127.3
Be	NA	97.4	93.9	NA	99.1	95.8

more weakly bound interactions. The Be-N stretch in cyclic 1-Be cyclic is higher compared to that in cyclic 2-Be (892.5 and 880.2 cm^{-1} , respectively) — consistent with a stronger interaction in the former. Likewise the C-Be stretch is higher in cyclic 1-Be compared to the analogous stretch in cyclic 2-Be (665 and 595 cm^{-1} , respectively). In olefin and conjugated models without carbonitrile functionality, similar trend is observed — the C-Be bond stretch in Be(II)-ethylene (721.5 cm^{-1}) is 60 cm^{-1} lower (weaker interaction) compared with that in butadiene (781.9 cm^{-1}) conjugated model. The Mg-N and Ca-N bond stretches much weaker compared to Be-N (481.6 and 390.4 cm^{-1} , respectively) that contributed to low dissociation energy obtained later.

Electron population analysis

The C4 atom in 2-cyanobutadiene (receptor 1) utilizes its 2s, $2p_x$, and $2p_y$ orbitals to form sp^2 hybrid orbitals used to form covalent bonds with C3 and two hydrogen atoms. The $2p_z$ orbital remains for formation of π -bond with C3. The electron population of the $2p_x$ and $2p_y$ orbitals in C4 are greater than

one due to contributions from neighboring C3 and two hydrogen atoms. Interaction with Be(II) causes migration of electron density from the C3-C4 π -bond to the C4 carbon center, rehybridizes the carbon orbitals to sp^3 -like and significantly increased the C4 $2p_y$ and $2p_z$ population by 25 and 28 %, respectively. This observation is in keeping with a significant reduction in C3 population upon formation of cyclic 1-Be, the whole population of C3 is reduced by about 10 %, and the C3 $2p_z$ orbital alone experiences a 35 % reduction in population and thus becomes a cationic center (Table 6). The observed electron population data are in good accord with the GIAO NMR shieldings data described earlier. The *s* versus *p* characters by percentage in Table 7 further support the rehybridization arguments. The C4 center significantly exhibits reduced *s* character and increased *p* character in cyclic 1-Be and the interaction between C4 and Be(II) involve sp^3 -like orbital.

The C3 center experience a slight increase in *p* character presumably to better stabilize the positively charge carbon. On the contrary, the C3 and C4 atoms show negligible changes in the acyclic 1-Be complex.

Table 5 Vibrational frequencies of Be-N and Be-C_{vinyl}

a) Be-N _{cyano} bond stretch (cm^{-1})		
CH ₃ -CN—Be		792.4
H-CN—Be		970.7
CH ₂ CHCN—Be		816.7
acyclic 2-Be(II)		800.5
cyclic 2-Be(II)		880.2
acyclic 1-B (II)		884.3
cyclic 1-Be(II)		892.5
cyclic 1-Mg(II)		481.6
cyclic 1-Ca(II)		390.4
b) Be-C _{vinyl} bond stretch (cm^{-1})		
cyclic 1-Be(II)		665.0
cyclic 1-Mg(II)		359.1
cyclic 1-Ca(II)		109.6
cyclic 2-Be(II)		595.0
CH ₂ CH ₂ —Be		721.5
CH ₂ CH CH CH ₂ —Be		781.9

Frontier molecular orbital analysis

The cyclic 1-Be complex requires interactions between Be(II) with carbonitrile N6 and C4 atoms (Scheme 1). The frontier orbital analysis indicates the HOMO-3 in 2-cyanobutadiene (receptor 1) most probably is utilized in forming the cyclic 1-Be complex. This MO has suitable orbital to be occupied by lone electron pair on the cyano nitrogen atom (N6), and a $2p$ orbital on C4 that can be utilized to form interactions with beryllium cation. Furthermore, the same phase of the orbitals are pointing toward Be(II). The cyano N6 atom presumably exhibits significant 2s orbital and initially interacts with Be(II). In the next step, due to stabilization gained in further transfer of positive charge from Be(II) to the receptor, the $2p$ orbital on C4, having the same phase as that in N6, forms a bridge with the vinylic carbon terminal and thus affords the six-membered ring. The low-lying unoccupied molecular orbitals are of interest in nucleophilic addition to the cyclic complex by Lewis bases and in polymerization process

Table 6 NBO populations of 2-CN BD and Be(II)- 2-CN BD

2-CN BD				
	2s	2p _x	2p _y	2p _z
C3	0.976	1.054	1.191	1.013
C4	1.066	1.214	1.145	0.963
C5	0.854	0.945	0.965	0.925
N	1.594	1.231	1.363	1.094
Be(II)- 2-CN BD				
C3	1.028	1.060	1.083	0.658
C4	1.172	1.168	1.433	1.232
C5	0.883	0.880	0.784	0.817
N	1.518	1.455	1.298	1.236

involving beryllium catalysts. The FMO of the cyclic 1-Be complex shows that the energies of the low-lying unoccupied MO's in ascending order are assigned to those in C3-C4, C1-C2, and C5-N6, respectively (Fig. 4). Therefore, nucleophilic addition to the C3 cation center is energetically favorable based on FMO argument.

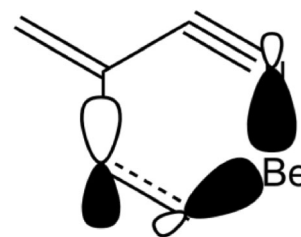
Energetics of divalent complexes

Accuracy on calculated G3 energies used to deduce relative stability of beryllium(II) adducts with unsaturated carbonitrile receptor models have first been verified using experimental (NIST) heats of formation [15]. The following reactions involving hydrogenation of beryllium(II) oxide and fluorination of beryllium(I) hydride and beryllium atom are employed to determine G3 error in calculating energies of beryllium compounds (Table 8).

The results show that G3 reproduces the experimental heats of reaction for reactions 1, 2, and 3 within experimental error (4.8, 1.9, and 1.5 kcal mol⁻¹, respectively). It should be noted that experimental data for beryllium compounds are old and limited in number and could be inaccurate. The effectiveness of interactions between beryllium(II) and the carbonitrile receptor models and simpler models are estimated by the

Table 7 Percentages of *s* versus *p* characters in C3-C4 and C5-N6 σ -bonds in 2-CN BD and Be(II)- 2-CN BD

C3-C4 σ -bond <i>s</i> and <i>p</i> characters by percentage				
	C3 <i>s</i>	C3 <i>p</i>	C4 <i>s</i>	C4 <i>p</i>
2-CN BD (1)	38.9	61.0	38.3	61.7
Cyclic 1-Be	37.1	62.9	31.2	68.8
Acyclic 1-Be	39.4	60.6	37.3	62.6
C5-N6 σ -bond <i>s</i> and <i>p</i> characters by percentage				
	C5 <i>s</i>	C5 <i>p</i>	N6 <i>s</i>	N6 <i>p</i>
2-CN BD (1)	47.6	52.4	45.3	54.4
Cyclic 1-Be	45.7	54.3	45.9	53.8
Acyclic 1-Be	43.0	56.9	59.2	40.7

**Scheme 1** Interaction between C4 and Be

relative stabilization of doubly charged and naked beryllium cation by the ligands. Stabilization of beryllium(II) by one molecule of water in Be(II)-H₂O is used as a reference for zero energy. Roughly this reflects the ability of the neutral model molecules in stabilizing doubly charged beryllium. G3 results (Table 9) show that individual contribution of one ethylene is negligible (destabilization by 2 kcal mol⁻¹) and comparable to one water molecule. Quite on the contrary, one molecule of acetonitrile model affords 44.4 kcal mol⁻¹ stabilization. Conjugation effect in acrylonitrile gives 52.1 kcal mol⁻¹ stabilization or 7.7 kcal mol⁻¹ additional stability when compared to Be(II)-CH₃CN. Likewise, in unsaturated carbonitrile models 2-CN BD when there is no vinyl participation (in the acyclic complex) the stabilization energy is reduced by 9.7 kcal mol⁻¹. The presence of conjugation due to one diene moiety in 2-CN BD gives additional stability of 6.6 kcal mol⁻¹ compared to the analogous cyclic Be(II)-3- CN P complex.

Our computational results reveal that cyclic complexes between 2-cyanobutadiene (receptor 1) and Be(II), Mg(II), and Ca(II) are all bound in the gas phase (Table 10). We initially thought that only the cyclic adduct of Be(II) is important.

In the later part of this work comparison in binding strengths between carbonitrile receptor and group II divalent cations became more critical. Consequently, the G4 method that covers calcium utilizing Dunning's correlation consistent aug-cc-pVnZ basis sets, were employed to determine binding energies for complexes involving Be(II), Mg(II), and Ca(II). G4 calculations show that formation of the cyclic 1-Be is 46 % more exothermic than that of cyclic 1-Mg. Likewise, while the formation of cyclic 1-Ca is still exothermic by -76.9 kcal mol⁻¹, but it is 35 % less exothermic compared to the Mg(II) complex.

Table 8 Benchmark reactions involving beryllium compounds (G3 and NIST energies in kcal mol⁻¹)

	NIST ΔH	G3 ΔH_{rxn}	Error
BeO + H ₂ → Be + H ₂ O rxn 1	-13.0	-17.8	4.8
BeH + F ₂ → BeF + HF rxn 2	-187.4	-185.5	1.9
Be + F ₂ → BeF ₂ rxn 3	-267.7	-266.2	1.5

Table 9 Beryllium(II) dissociation energies involving Be(II) complexes as measure of stabilization by receptor models; using one water molecule as a reference

Complex	G3 ΔH_{rxn} (kcal mol ⁻¹)
1 (H ₂ O)-Be ²⁺ → Be ²⁺ + H ₂ O	-142.8
2 (H ₂ O) ₂ -Be ²⁺ → Be ²⁺ + 2H ₂ O	-260.3
3 CH ₂ =CH ₂ -Be ²⁺ → Be ²⁺ + CH ₂ =CH ₂	-140.8
4 CH ₃ -CN-Be ²⁺ → Be ²⁺ + CH ₃ -CN	-187.2
5 CH ₂ CHCN-Be ²⁺ → Be ²⁺ + CH ₂ =CHCN	-194.9
6 CH ₃ -CN-Be ²⁺ -CH ₂ CH ₂ → Be ²⁺ + CH ₃ -CN CH ₂ CH ₂	-280.7
7 3-CN P-Be ²⁺ (acyclic) → Be ²⁺ + 3-CN P	-208.8
8 3-CN P-Be ²⁺ (cyclic) → Be ²⁺ + 3-CN P	-194.8
9 2-CN BD-Be ²⁺ (acyclic) → Be ²⁺ + 2-CN BD	-199.1
10 2-CN BD-Be ²⁺ (cyclic) → Be ²⁺ + 2-CN BD	-215.4

Overlap population analysis

Overlap population between two interacting centers and atomic valence on the central atoms in molecular fragments indicate the importance of valence type interaction or electron-sharing type chemical bonding as opposed to ionic interaction. We utilize AOMix program by S. Gorelsky to obtain individual atom-metal spin, total spin, and metal atomic valence populations [19].

Although the C4-Be bond distance (1.78 Å) in cyclic 1-Be is longer than that in N6-Be (1.61 Å) (refer to Fig. 2), the former shows significantly higher overlap population (0.462) compared to the later (0.140) (Table 11). This observation is presumably due to the high electronegativity of nitrogen atom that keeps its lone electron pair close to its nuclei and not in the overlap area. On the contrary, the rehybridized C4 (from *sp*² to *sp*³-like) shows significant migration of electron population from the C3-C4 π -bond to the covalent-type C4-Be overlap area. The interaction between Be(II) and 3-cyanopropene (receptor 2) shows similar pattern of carbon versus nitrogen overlap population.

Mg(II) shows more balanced overlap population with carbon and nitrogen terminals in both unsaturated carbonitrile receptor models 1 and 2. Ca(II) exhibits predominantly ionic type interaction and has only less than one electron in its atomic valence (Table 11). Both Be(II) and Mg(II) show

Table 10 G4 dissociation energies of 2-cyanobutadiene complexes with Be(II), Mg(II), and Ca(II)

Complexes	G4 ΔH_{rxn} (kcal mol ⁻¹)
2-CN BD-Be ²⁺ → Be ²⁺ + 2-CN BD (cyclic)	-216.1
2-CN BD-Mg ²⁺ → Mg ²⁺ + 2-CN BD (cyclic)	-117.6
2-CN BD-Ca ²⁺ → Ca ²⁺ + 2-CN BD (cyclic)	-76.9

Table 11 Metal valence and overlap population analysis

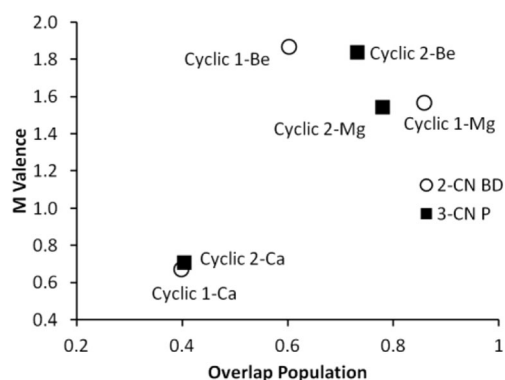
	M valence	C-M spin	N-M spin	Total spin
Cyclic 1-Be	1.870	0.462	0.140	0.602
Cyclic 1-Mg	1.570	0.396	0.462	0.858
Cyclic 1-Ca	0.673	0.124	0.274	0.398
Cyclic 2-Be	1.838	0.454	0.278	0.732
Cyclic 2-Mg	1.543	0.352	0.428	0.780
Cyclic 2-Ca	0.707	0.142	0.262	0.404

consistently high atomic valence (greater than 1.5) involved in formation of cyclic complexes (Fig. 5).

Transition structure

In order to locate the structures of the transition states we use the synchronous transit-guided quasi-Newton method utilizing Gaussian 09 QST2 keyword, wherein the acyclic structure (acyclic 1-Be) had been designated as the reactant and the cyclic structure (cyclic 1-Be) as the product. One imaginary frequency at -220.8 cm⁻¹ has been located that corresponds to the transition state. Formation of the acyclic complex between Be(II) and 1 in the gas phase is exothermic by 213.3 kcal mol⁻¹. Interaction between Be(II) and C4 gives additional stabilization by 12.5 kcal mol⁻¹ and thus gives rise to the cyclic complex (Fig. 6).

Intrinsic reaction coordinate (IRC) result confirms that the transition structure which has a forward activation barrier of 12.3 kcal mol⁻¹ connects the two optimized minima. In further solvent effect studies utilizing the IEFPCM continuum model, that are not described in details in this report, we found that the cyclic complex (cyclic 1-Be) survives non-polar solvents such as heptane, benzene, and dichloromethane. However, polar solvents such as diethyl ether and tetrahydrofuran were found to stabilize Be(II) and break the Be(II)-C4 bond, and the cyclic complex ring opens to the acyclic form.

**Fig. 5** Plot of metal atomic valence versus overlap population in complexes between Be(II), Mg(II), and Ca(II) with 2-CN BD and 3-CN P

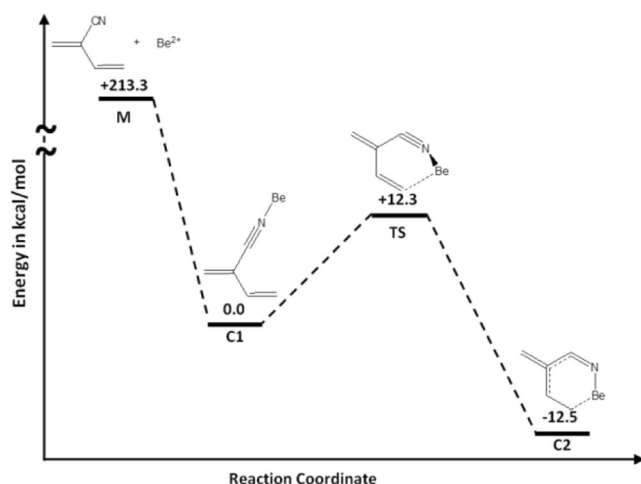


Fig. 6 Energy profile of 2-CN BD and its complexes with Be(II)

Rational for beryllium(II) recognition using unsaturated carbonitriles

Our results suggest that beryllium cation interacts with unsaturated carbonitrile initially by forming N-Be bond. The interaction between Be(II) and the cyano nitrogen atom is more than 45 kcal mol^{-1} stronger than that with vinyl carbons, using the acetonitrile and ethylene simple models and examined separately (Table 9). Moreover, the energetics data reveal that interaction with the vinyl carbon to form cyclic 1-Be further the complex by 12 kcal mol^{-1} . Furthermore, G4 results show that Mg(II) and Ca(II) are also capable of making interaction with vinyl carbon, after forming acyclic complexes through N-Be bonding. Consequently, it is important to investigate if a complex between Be(II) and a conjugated carbonitrile could still form another interaction with a separate vinyl moiety. For this purpose we investigate the complex between Be(II) and two separate fragments; acrylonitrile and ethylene, and the results confirm that Be(II) complexes with fragmented conjugated carbonitrile and vinyl moiety are bound. The optimized structures show that the Be-C bond distance in the simple model (1.777 \AA) is very similar to that in cyclic 1-Be (1.78 \AA). On the contrary, the Be-N bond length in the fragmented simpler model (1.54 \AA) is significantly shorter than that in cyclic 1-Be (1.61 \AA). This presumably is due to the ring strain in the acyclic 1-Be six-membered complex. The π -network results in a strained planar structure, except for the dihedral angle involving the sp^3 -like C4 center that could not adopt a less strained chair conformation. The acyclic 1-Be exhibits even shorter Be-N bond distance (1.48 \AA). This could be explained in terms of more efficient interaction between Be(II) and only one ligand, the imparted positive charge delocalized by the conjugated carbonitrile receptor, and the resulting acyclic complex free from ring strain. The C4 in cyclic 1-Be exhibits more significant rehybridization to sp^3 -like center

having H-C4-H bond angle of 110.8° compared to 116.7° in the fragmented simple models.

We have reported earlier that saturated carbonitrile can be used to recognize metal cations [16, 17]. Optimized geometries indicate that in unconjugated carbonitriles, interaction with cations leaves the cyano bond unaffected (Fig. 7). However, stabilization due to π -network in conjugated carbonitriles strongly suggests formation of ketenimine reactive functionality and significant reduction of the C-N bond order [18]. In our previous study [20], we have found that interactions between carbonitrile-carboxaldehyde receptor models and group I and II cations can be elucidated using electron sharing versus ionic interaction approach. The results reveal that electron sharing by uncharged heteroatom receptors favors divalent cations, and group I cations can be effectively discriminated utilizing this approach. Moreover, magnesium exhibits significantly higher atomic valence compared to calcium. Therefore, calcium can be discriminated in highly selective magnesium determination based on electron sharing ground [21]. However, lacking in valence electron but retaining its positive charge, calcium can be selectively determined using multiple negatively charged receptors. In addition, being more weakly hydrated, calcium is favored by the Hofmeister effect [22, 23]. Beryllium recognition follows similar line of reasoning as that described for magnesium. In all cases it exhibits similar nature of interactions with receptor models; carbonitriles, carboxaldehyde, polyether, and vinyl carbon [24] in particular. Preferential recognition toward beryllium is expected with uncharged ionophores, having multiple ligands and having suppressed Hofmeister effect [22, 23]. Judicial choice of polymeric sensing membrane, lipophilic borate, and plasticizer that reduces ion exchanging characteristics can further favor beryllium [25, 26].

Computational details

Calculations were performed with a Gaussian 09 program package [27]. All calculations were performed with B3LYP using the split valence basis set with polarization and diffuse

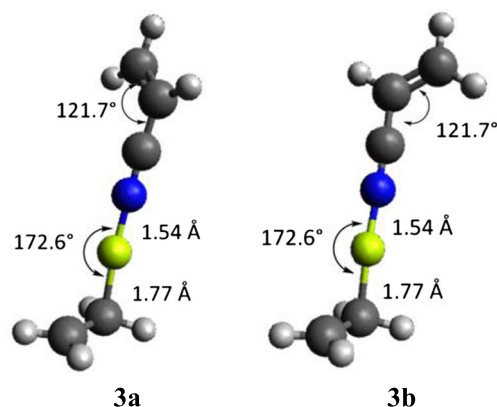


Fig. 7 Optimized geometries of simple models

functions for heavy atoms. The Becke three parameter hybrid functionals have been employed for a wide variety of applications. The functionals have the form devised by Becke in 1993 [28, 29] (Eq 1)

$$A * E_X^{Slater}(-A) * E_X^{HF} B * \Delta E_X^{VWN} C * \Delta E_C^{non-local} \quad (1)$$

:

where A , B , and C are 0.20, 0.72, 0.81, respectively, constants determined via fitting to the G1 test set.

There are several variations of this hybrid functional. B3LYP uses the non-local correlation provided by the LYP expression, and VWN functional III for local correlation (not functional V). Note that since LYP includes both local and non-local terms, the correlation functional used is actually:

$$C * E_C^{LYP}(1-C) * E_C^{VWN} \quad (2)$$

.

In other words, VWN is used to provide the excess local correlation required, since LYP contains a local term essentially equivalent to VWN[30].

All geometry optimization are initially obtained at the B3LYP/6-31+G** level [29, 31, 32] for non-metal and QZVP [33, 34] for metal. Gaussian NBO version 3.1 has been utilized to calculate atomic orbital occupancies and its contribution to bonding interaction and delocalization of electron density within the models and beryllium(II) complexes [35]. The ^{13}C NMR isotropic shielding was calculated with the GIAO method using the optimized structures obtained from DFT calculation [36]. The G3 method is employed to estimate relative stability of various beryllium(II) complexes with receptor models and deduce the ability of the models in stabilizing naked doubly charged beryllium. Accuracy of G3 energy calculations in dealing with beryllium compounds has been benchmarked with NIST experimental heats of formation of beryllium atom, beryllium(I) hydride, beryllium (I) fluoride, and beryllium(II) fluoride[37]. G3 geometry optimization[38, 39] is done at MP2 level using 6-31G basis set and the structure is used to calculate harmonic frequencies and for all subsequent calculations. The final MP2 calculations use a larger basis (G3large) and both the core and valence electrons are correlated. The [quadratic configuration interaction](#) calculation with single, double, and triples excitation contribution (QCISD(T)) [40] was done for the correction for correlation effects beyond a fourth-order perturbation theory. Additional core correlation corrections are included through a spin-orbit and valence electron empirical correction. Different empirical parameters are also introduced in the higher level correction (HLC) [15]. The Gaussian-4 theory is the improvement over G3 theory with mean absolute

deviation of $0.83 \text{ kcal mol}^{-1}$ from experiment for the comprehensive collection of 454 energies (for main group molecules) in the G3/05 test set [41]. G4 theory uses B3LYP/6-31G(2df,p) for structure optimization, harmonic frequency, and all subsequent calculations [42]. Hartree-Fock energy limit E (HF/limit) is determined using two-point extrapolation scheme and Dunning's aug-cc-pVnZ basis sets. For correlation correction beyond the fourth-order perturbation theory, CCSD(T)/6-31G* is used instead of QCISD(T)/6-31G* (in G3). The HLC has the same form as in G3 but with two additional parameters. The AOMix package was utilized to analyze the nature of the chemical bonding in analyte-receptor interaction by extracting the electron sharing components in the overlapping area and quantifying the atomic valence of metal centers [19, 43].

Conclusions

Beryllium(II) recognition molecules have been designed using DFT and G3 computational methods. 2-Cyanobutadiene and 3-cyanopropene represent unsaturated carbonitrile models, with and without π -system. Small molecule models such as ethylene, acetonitrile, and acrylonitrile elucidate individual participation and cumulative effect of vinyl and cyano functionalities in critical design parameters especially the strengths of the $\text{C}_{\text{vinyl}}\text{-Be}$ and $\text{Be-N}_{\text{cyano}}$ interactions. GIAO NMR shifts probed centers of positive charges in the models and beryllium(II) complexes. In all cases the changes in the degree of carbon nuclei shielding is consistent with the reasoning on how doubly charged beryllium imparts and distributes the donated positive charge. NBO analysis examined orbital occupancies that suggest rehybridization at the terminal vinyl carbon to sp^3 , forming interaction with beryllium atom and at the carbon and nitrogen atoms, adjusting to the positively charged centers. Beryllium(II) cyclic complexes with 2-CN BD and 3-CN P exhibit almost perfect planar, except for slight out of plane dihedral angle at one atom of the six membered ring. This and numerous other evidence suggest that both cyano and vinyl groups participate in binding with beryllium, and π -system conjugation in 2-CN BD affords 16.3 kcal mol stabilization. Relative stabilization by one water molecule, ethylene alone has negligible effect, whereas stabilization of unconjugated carbonitrile model (acetonitrile) gives rise to $44.4 \text{ kcal mol}^{-1}$ stabilization. The interaction of Be(II)-2 CN BD is the strongest compared against Mg(II) and Ca(II) complexes, proven by the dissociation energy obtained from G4 calculation. The Be(II)-2-CN BD complexes of cyclic and acyclic forms separated by $12.3 \text{ kcal mol}^{-1}$ barrier height as shown by the QST2 method. Discrimination of Ca(II) from Be(II) and Mg(II) can be based

on the overlap population analysis that showed Ca(II) prefers ionic interaction with the receptor models.

Acknowledgments This work is fully funded by the Research Grant UM-MOE UM.C/625/1/HIR/MOE/F00004-21001 from the Ministry of Education Malaysia and University Malaya Research Grant-Program (UMRG-Project No. RP006B-13SUS and RP012B-14SUS). The authors would like to thank Ministry of Education (MOE) and Ministry of Science, Technology and Innovation (MOSTI), Malaysia for their supports.

References

- Everest DA (1964) The chemistry of beryllium. Elsevier Pub. Co
- Watanabe F, Kasai A (1995) Low outgassing residual gas analyzer with a beryllium-copper-alloy-flanged ion source. *J Vac Sci Technol A* 13(2):497–500
- Mooradian VG (1952) Clad beryllium-copper alloys. Washington, DC: Patent U.S. Patent No. 2,608,753
- Wang X, Wang R, Peng C, Li T, Liu B (2011) Growth of BeO nanograins synthesized by polyacrylamide Gel route. *J Mater Sci Technol* 27(2):147–152
- Swinen S, Nguyen VS, Nguyen MT (2010) Catalytic generation of molecular hydrogen from hydrazine using lithium and beryllium hydrides. *Chem Phys Lett* 496(1):25–31
- Kobetz P, Laran RJ, Johnson RW Jr (1974) Process for the manufacture of beryllium hydride. Washington, DC: Patent US Patent 3:832, 456
- Executive HaS (2003) Beryllium and you. Working with beryllium — are you at risk? United States
- Binkley JS, Seeger R, Pople JA, Dill JD, Schleyer PR (1977) Carbon-beryllium binding in CH₂Be. *Theor Chim Acta* 45(1):69–72
- Swope WC, Schaefer HF III (1976) Model organometallic systems. The interaction of 2S beryllium (1+) ion, 1S beryllium, and 3P beryllium atoms with acetylene and ethylene. *J Am Chem Soc* 98(25):7962–7967
- Lao RC, Riter JR Jr (1967) Estimate of the total energy of the beryllium hydride molecule. *J Phys Chem* 71(8):2737–2739
- Parameswaran P, Frenking G (2009) Chemical bonding in transition metal complexes with beryllium ligands [(PMe(3)) (2)M–BeCl(2)], [(PMe(3)) (2)M–BeClMe], and [(PMe(3)) (2)M–BeMe(2)](M=Ni, Pd, Pt)†. *J Phys Chem A* 114(33):8529–8535
- Alex A, Hänsele E, Clark T (2006) The ethylene/metal (0) and ethylene/metal (I) redox system: model ab initio calculations. *J Mol Model* 12(5):621–629
- Hirai A, Nakamura M, Nakamura E (1999) Synergetic dimetallic effects in Gaudemar/Normant coupling between allylzinc and vinyl Grignard reagents. *J Am Chem Soc* 121(37):8665–8666
- Hirai A, Nakamura M, Nakamura E (2000) Mechanism of addition of allylmetal to vinylmetal. Dichotomy between metallo-Ene reaction and metalla-claisen rearrangement. *J Am Chem Soc* 122(48):11791–11798
- Namazian M, Zakery M, Noorbala MR, Coote ML (2008) Accurate calculation of the pKa of trifluoroacetic acid using high-level ab initio calculations. *Chem Phys Lett* 451(1):163–168
- Rosli AN, Bakar MAA, Manan NSA, Woi PM, Lee VS, Zain SM, Ahmad MR, Alias Y (2013) G3 assisted rational design of chemical sensor array using carbonitrile neutral receptors. *Sensors* 13(10):13835–13860
- Rosli AN, Ahmad MR, Woi PM, Bakar MAA, Manan NSA, Zain SM, Alias Y, Lee VS, Maluin FN (2013) Accurate computational approach for designing cation recognition molecules. In: The 6th International Conference on Sensors, Melaka, p 68
- Rosli AN, Bakar MAA, Manan NSA, Woi PM, Lee VS, Zain SM, Ahmad MR, Alias Y (2014) Does cation break the cyano bond? A critical evaluation of nitrile-cation interaction. *J Mol Model* doi:10.1007/s00894-014-2219-3
- Gorelsky SI (2013) AOMix: Program for Molecular Orbital Analysis. 6.85b edn
- Rosli AN, Bakar MAA, Lee VS, Zain SM, Ahmad MR, Manan NSA, Alias Y, Woi PM (2014) Rational design of carbonitrile-carboxaldehyde cation receptor models - probing the nature of heteroatom-metal interaction. *J Mol Model* 20:2428
- Zhang W, Spichiger UE (2000) An impedance study of Mg²⁺-selective membranes. *Electrochim Acta* 45(14):2259–2266
- Zhang Y, Cremer PS (2006) Interactions between macromolecules and ions: the Hofmeister series. *Curr Opin Chem Biol* 10(6):658–663
- Kherb J, Flores SC, Cremer PS (2012) Role of carboxylate side chains in the cation Hofmeister series. *J Phys Chem B* 116(25):7389–7397
- Marynick DS, Kirkpatrick CM (1988) Localized molecular orbitals of simple metal-olefin complexes. *J Mol Struct (THEOCHEM)* 169: 245–256
- Bakker E, Meruva R, Pretsch E, Meyerhoff M (1994) Selectivity of polymer membrane-based ion-selective electrodes: Self-consistent model describing the potentiometric response in mixed ion solutions of different charge. *Anal Chem* 66(19):3021–3030
- Bakker E, Pretsch E, Bühlmann P (2000) Selectivity of potentiometric ion sensors. *Anal Chem* 72(6):1127–1133
- Frisch M, Trucks G, Schlegel H, Scuseria G, Robb M, Cheeseman J, Scalmani G, Barone V, Mennucci B, Petersson G, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov, Bloino J, Zheng G, Sonnenberg JL, Hada, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, T. Nakajima AF, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery JA, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Keith T, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas O, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2010) Gaussian 09, Revision C. 01. Gaussian Inc, Wallingford
- Becke AD (1993) A new mixing of hartree-fock and local density-functional theories. *J Chem Phys* 98(2):1372–1377
- Lee C, Yang W, Parr RG (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys Rev B Condens Matter* 37(2):785–789
- Vosko SH, Wilk L, Nusair M (1980) Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. *Can J Phys* 58(8):1200–1211
- Hratchian H, Schlegel H (2005) Using Hessian updating to increase the efficiency of a Hessian based predictor-corrector reaction path following method. *J Chem Theory Comput* 1(1):61–69
- Becke AD (1988) Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys Rev A* 38(6):3098
- Weigend F, Ahlrichs R (2005) Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: design and assessment of accuracy. *Phys Chem Chem Phys* 7(18): 3297–3305
- Weigend F, Furche F, Ahlrichs R (2003) Gaussian basis sets of quadruple zeta valence quality for atoms H–Kr. *J Chem Phys* 119: 12753
- Glendening E, Reed A, Carpenter J, Weinhold F (1988) NBO, version 3.1. Madison, WI
- Cheeseman JR, Trucks GW, Keith TA, Frisch MJ (1996) A comparison of models for calculating nuclear magnetic resonance shielding tensors. *J Chem Phys* 104(14):5497–5509

37. Chase MW, Force JANA (1998) NIST-JANAF thermochemical tables
38. Curtiss LA, Raghavachari K, Redfern PC, Rassolov V, Pople JA (1998) Gaussian-3 (G3) theory for molecules containing first and second-row atoms. *J Chem Phys* 109: 7764–7776
39. Pickard FC, Griffith DR, Ferrara SJ, Liptak MD, Kirschner KN, Shields GC (2006) CCSD (T), W1, and other model chemistry predictions for gas-phase deprotonation reactions. *Int J Quantum Chem* 106(15):3122–3128
40. Curtiss LA, Raghavachari K (2002) Gaussian-3 and related methods for accurate thermochemistry. *Theor Chim Acta* 108(2):61–70
41. Curtiss LA, Redfern PC, Raghavachari K (2011) Gn theory. *Wiley Interdisciplinary Reviews: Comput Mol Sci* 1(5):810–825
42. Curtiss LA, Redfern PC, Raghavachari K (2007) Gaussian-4 theory. *J Chem Phys* 126:084108–084119
43. Gorelsky S, Lever A (2001) Electronic structure and spectra of ruthenium diimine complexes by density functional theory and INDO/S. Comparison of the two methods. *J Organomet Chem* 635(1):187–196