Estimations of Fe$^{0/−1}−\text{N}_2$ interaction energies of iron(0)-dicarbene and its reduced analogue by EDA-NOCV analyses: crucial steps in dinitrogen activation under mild conditions†

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Metal complexes containing low valence iron atoms are often experimentally observed to bind with the dinitrogen (N$_2$) molecule. This phenomenon has attracted the attention of industrialists, chemists and bio-chemists since these N$_2$-bonded iron complexes can produce ammonia under suitable chemical or electrochemical conditions. The higher binding affinity of the Fe-atom towards N$_2$ is a bit ‘mysterious’ compared to that of the other first row transition metal atoms. Fine powders of α-Fe$^0$ are even part of industrial ammonia production (Haber–Bosch process) which operates at high temperature and high pressure. Herein, we report the EDA-NOCV analyses of the previously reported dinitrogen-bonded neutral molecular complex (cAAC$^0$)$_2$Fe$^0$−N$_2$ (1) and mono-anionic complex (cAAC$^−$)$_2$Fe$^{−1}$−N$_2$ (2) to give deeper insight of the Fe−N$_2$ interacting orbitals and corresponding pairwise intrinsic interaction energies (cAAC$^=$ = cyclic alkyl(amino) carbene; R = Dipp or Me). The Fe$^0$ atom of 1 prefers to accept electron densities from N$_2$ via σ-donation while the comparatively electron rich Fe$^{−1}$ centre of 2 donates electron densities to N$_2$ via π-backdonation. However, major stability due to the formation of an Fe−N$_2$ bond arises due to Fe $\rightarrow$ N$_2$ π-backdonation in both 1 and 2. The cAAC$^=$ ligands act as a charge reservoir around the Fe centre. The electron densities drift away from cAAC ligands during the binding of N$_2$ molecules mostly via π-backdonation. EDA-NOCV analysis suggests that N$_2$ is a stronger π-acceptor rather than a σ-donor.

Introduction

Different forms of energy can be argued as the ingredients of life.$^1$ Energy, life and information are linked to each other.$^2$ Nitrogen is one of the most common and most essential elements for the sustainability of living organisms, plants and animals. The earth’s atmosphere is mostly dominated (78%) by dinitrogen gas (N$_2$) and yet most of the living organisms, plants and animals cannot directly utilize it according to their needs.$^3$ This is due to the extreme inertness and non-polar nature of kinetically stable N$_2$ molecules. The reduction of N$_2$ to ammonia (NH$_3$) and/or to other forms of N-containing compounds such as amino acids, nucleoside, nucleotides and most importantly peptides are keys to the existence of life on earth.$^4$ Thermodynamically, reduction of areal N$_2$ to relatively more stable NH$_3$ is exothermic (−46 kJ mol$^{-1}$ at 298 K). However, the binding of N$_2$ and followed by activation of the N≡N bond is challenging to chemists and bio-chemists. Interestingly, a few microorganisms in the nature have found a way to solve the problem$^5$ providing around hundred twenty megatons of nitrogen source per year by nitrogen fixation. It is associated with some leguminous plants, like clover, beans, peas, alfalfa, lentils and lupins.$^6$ The enzyme called nitrogenase possesses a bimetallic inorganic core V/ Mo−Fe$_5$S$_6$C$^{−1}$ (co-factor) which is responsible for N$_2$ binding in the reduced state.$^7,8$ It catalytically produces ammonia via reductive protonation either by ‘distal’ or ‘alternative’ pathways with the loss of hydrogen gas during this process.$^7,8$ The exact nature and mode of the dinitrogen binding and activation have not yet fully clear. N-containing nutrients are essential for the human race on the earth. Humans adopted domestic cultivation as early as 10 000 BC.$^9$ Fertilizers are now-a-days a must for effective cultivation. More than a century ago, Haber originally utilized an osmium catalyst under high temperature and pressure to produce 125 mL of NH$_3$ per hour.$^{10}$ In the following years Bosch and Mittasch developed efficient Fe$_3$O$_4$/FeO/α-Fe$^0$ catalyst with high surface area for industrial production of twenty tonnes of NH$_3$ per day in the next year at BASF company.$^{16,11}$ The catalytic efficiency of iron is further promoted with K$_2$O, CaO, SiO$_2$, and Al$_2$O$_3$. At present global annual production rate of ammonia is 174 million tonnes.$^{12}$ The actual Mittasch’s catalyst (Fe$_3$O$_4$/FeO/
α-Fe⁰ (Scheme 1) in Haber–Bosch catalytic cycle is the outer surface (α-Fe⁰) of very reactive Fe₃O₄/FeO/α-Fe⁰ particles having a body centre cubic (bcc) structure with two singly-occupied dₚ and dₓᵧ₋ᵧ orbitals which do not participate in multicentre delocalized bonding with its neighbouring Fe⁰ atoms.¹¹

To obtain a favourable thermodynamic driving force for the reaction between N₂ and H₂ the industrial process is designed to occur at high pressure (Scheme 1). In 2007 Gerhard Ertl has been awarded the Nobel Prize in chemistry for his captivating decades long works on fundamental processes at the gas–solid interface involving Fe⁰–N₂ adsorption on the α-Fe⁰ surface of Fe₃O₄/FeO/α-Fe⁰ catalyst. His work on ‘Interaction of nitrogen with iron surfaces’ clarified the long-standing confusion in Haber–Bosch process.¹⁴ It has been found that N≡N bond dissociates on pure Fe-surfaces forming Fe₄N atomic-bilayer just above room temperature. He also explained the role of promoter K₂O in Haber–Bosch ammonia synthesis process employing photoelectron spectroscopy and other experimental techniques. The pre-adsorbed potassium on the Fe-surface removes energy barrier of dissociative nitrogen chemisorption of N₂ molecule.¹⁵ The overall yield of NH₃ in Haber–Bosch industrial process is 97% when the unreacted gases are recycled again and again.¹⁶ However, at present this process consumes ~2% of the total global energy supply. Additionally, it produces large amounts of greenhouse gases.¹⁸ Alternative synthetic methods which will produce NH₃ in a much greener way are highly desired.³⁷–⁴¹ Low valence and/or low valent metal complexes¹⁷–¹³,³⁷–⁴¹ and low coordinate boron–carbene¹⁴–³⁶ compounds are found to bind to N₂ which can be activated to obtain NH₃ or N₂H₄ under milder conditions.³⁷–⁴¹ The reductive protonation of bonded N₂ of these complexes can lead to the formation of either NH₃ or N₂H₄ or even a mixture of both. Formation of ammonia is more common due to its higher chemical valence (EDA-NOCV)¹⁶ analysis of free N₂ revealed that 30% of the total interaction energy between two N-atoms is only contributed by electrostatic energy (ΔEₑ₉-born). The remaining 70% is orbital interaction energy (ΔEₖₑ₉-born) which is due to the covalent character of triple bond of N₂ with zero dipole moment.³⁴–³⁵ The Pauli repulsion energy (ΔEₚ₉-born) between two interacting N-atoms is quite high due to repulsion between the electron clouds with similar spins (N–N = 1.102 Å). The Wiberg bond order has been computed to be 3.03. The orbital interaction energy (ΔEₖₑ₉-born) is actually due to the covalent interactions in both σ(3σₛ²) + π(1πₓ) bonds. The former is 65.6% while the latter is nearly half (34.4%) of the former. They together (σ + π) give total orbital interaction energy (ΔEₖₑ₉-born).³⁴–³⁵ Point to be noted that degenerate π⁺-orbitals (1πₓ) of N₂, which are composed of pₓ and pᵧ atomic orbitals, are high lying in energies (1πₓ; LUMO). The LUMO+1 is σ⁺ orbital (3σₛ²) and HOMO is N–N σ orbital (3σₓ²) of N₂.³⁴–³⁵

Several metal complexes with low valence iron atoms containing coordinated N₂ have been synthesized, isolated and characterized by X-ray single crystal structure determination.¹⁸–²¹,²⁷–³¹,⁴⁰,⁴¹ Additionally, they have been studied by different spectroscopic methods to shed light on their electronic structures. NBO calculations have been carried out to correlate the N–N bond lengths with those of experimentally obtained values to give emphasis on weakening of N–N bond due to M → N₂ backdonation.¹⁸–²¹,²⁷–³¹,⁴⁰,⁴¹ However, there is till now no report on the exact nature of the M–N₂ bonds and on their corresponding interaction energies (M = Fe and other transition metal) of stable/isolable dinitrogen bonded metal complexes. Herein, we report on the DFT, NBO, QTAIM calculations and EDA-NOCV analysis of previously reported dinitrogen-bonded (cAAC₅⁸)₃Fe–N₂ (1) and (cAAC₅⁸)₂Fe¹⁻–N₂ (2) complexes⁴² to give a deeper insight into the nature of M–N₂ bonds and corresponding pairwise interaction energies (cAAC₅⁸ = cyclic alky(amo) carbene; R = Dipp⁴³ or Me for our theoretical studies). The role of non-innocent cAAC ligands has also been discussed here.

Results and discussion

The spin of each Fe-atom of ferromagnetic α-iron metal is S = 1.¹⁰ The spin ground state of (cAAC¹⁰PP)₃Fe⁰ has been confirmed to be S = 1 by EPR and ⁵⁷Fe Mössbauer spectroscopy by Peters et al.⁴² Additionally, they have experimentally shown⁴¹ (by UV/vis
spectroscopy) that the $N_2$ binds to (cAAC)$_2$Fe$^0$ in end-on fashion. This $N_2$ binding at Fe-centre is highly temperature sensitive ($< -80 \, ^\circ C$).\textsuperscript{41} Experimentally the authors have isolated the elusive anionic (cAAC$^{Dipp}$)$_2$Fe$^{-1}$-$N_2$ species by reducing in situ formed precursor (cAAC$^{Dipp}$)$_2$Fe$^0$-$N_2$ (1') with KC$_8$ in the presence of 18-crown-6 ether below $-95 \, ^\circ C$ with the chemical composition of [(cAAC$^{Dipp}$)$_2$Fe(N$_2$)][K(18-crown-6)] (2') (Scheme 3). The latter species (2') has a ground state $S = \frac{1}{2}$ confirmed by solution EPR measurements.\textsuperscript{41} This anionic complex has further been shown to catalytically produce NH$_3$ below $-95 \, ^\circ C$.

The reduction of dinitrogen to ammonia takes place upon treatment with N$_2$, KC$_8$ and HBA$^7$·2Et$_2$O in ether medium. Only a little has been reported about their (1'-2') aspects of chemical bonding.\textsuperscript{41}

We have modelled and optimized (L)$_2$Fe$^0$-$N_2$ as neutral (1; L = cAAC$^{Me}$) and anionic complexes (2; L = cAAC$^{Me}$) stabilized by cAAC$^{Me}$ ligands to shed light on the bonding and stability of spectroscopically observed elusive neutral (cAAC$^{Dipp}$)$_2$Fe$^0$-$N_2$ (1'; cAAC$^{Dipp}$) and crystallographically characterized [(cAAC$^{Dipp}$)$_2$Fe$^{-1}$(N$_2$)][K(18-crown-6)] complexes (2') reported by

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**Scheme 2** End-on interactions between the orbitals metal (M) and N$_2$.

**Scheme 3** Representative Fe–N$_2$ containing iron complexes.\textsuperscript{17,18,40,41,45}
Jonas Peters and co-workers. The Fe–N bond distance of [(cAACDipp)2Fe(N2)][K(18-crown-6)] is 1.777 Å while the N–N bond length of the bonded N2 is 1.035(4) Å which is slightly shorter than that of the free N2 (1.102 Å) molecule. X-ray crystallography of the complex revealed that Fe-centre adopted a distorted trigonal planar coordination geometry.

The modelled neutral (cAACMe)2Fe–N2 complex (1) has been optimized in singlet (Fig. S1†), triplet (Fig. 1) and quintet electronic states (Fig. S1†). The calculations at BP86-D3(BJ)/Def2TZVPP level of theory in the gas phase suggest that triplet state is more stable by 11.53 and 20 kcal mol\(^{-1}\) over singlet and quintet states, respectively. The N–C–C–N torsion angle of 37.7° in complex 1 suggests that the two cAAC ligands are relatively perpendicular to each other, while the C–Fe–C bond angle of 149.3° shows that the geometry is lightly bent compared to that of (cAAC)2Fe\(^0\) containing a two coordinate Fe\(^0\) atom at CcAAC–Fe–CcAAC bond angle of 169.52(5)°. The Fe–N and N–N bond lengths of the simplified complex 1 are 1.801 Å and 1.140 Å respectively (with Me-group on N-atom of cAAC ligand). The two cAAC ligands are almost equidistant from the central Fe atom with a minor difference (Fig. 1). In contrast to the Fe–Mo cofactor (FeMoco) of nitrogenase enzyme, the two coordinate (cAAC)Fe can bind to N\(_2\) even in resting condition below \(-80^\circ\) or in other words without the external supply of electrons.

Upon reduction, the geometry becomes more bent in complex 2 as indicated by the CcAAC–Fe–CcAAC bond angle of 117.4° (Fig. 1). This differs from the C–Fe–C bond angle (140.8°) of experimentally isolated [[(cAACDipp)2Fe(N2)][K(18-crown-6)]] (2') due to the steric effects of two cAACDipp ligands. We can reason the reduction in C–Fe–C bond angle in the modelled complex to the presence of less bulky substituents on cAAC ligand which reduces the steric repulsion. This reduction in C–Fe–C bond angle also slightly lower the C–Fe bond lengths in complex 2 compared to that of the reported structure. The Fe–N bond distance of modelled complex 2 (1.782 Å) correlated well with the reported value of 1.777 Å (2'). The geometrical parameters calculated at BP86-D3(BJ)/Def2TZVPP level agrees well with the experimental values with no major discrepancies. However, we have also performed geometry optimization of complexes 1 and 2 at the TPSS-D3(BJ)/Def2TZVPP and PW6B95-D3/Def2TZVPP level to compare and support the results. While

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Fig. 1  Optimized geometries of complex 1 in triplet state (s = 1) and mono-anionic complex 2 in doublet state (s = 1/2) at BP86-D3(BJ)/Def2-TZVPP level.
the Fe–N bond lengths of complexes 1 and 2 calculated at TPSS-D3(BJ) level are 1.808 Å, 1.782 Å respectively (Fig. S1†), the calculated N–N bond lengths are 1.136 and 1.149 Å (Fig. S1†). The geometrical parameters calculated at TPSS-D3(BJ) match well with the results of the BP86-D3(BJ) level. However, the Fe–N bond lengths (1.899 and 1.864 Å) calculated at PW6B95-D3 level (Fig. S1†) differ significantly with those calculated at TPSS-D3(BJ), BP86-D3(BJ) and also experimental values. The calculated C–Fe–C bond angle of complex 2 at TPSS-D3(BJ) is also acute (120.7°), supporting the reason for the difference from the experimental bond angle as mentioned above. The N–C–C–N torsion angle of 145.1° indicates that the two carbene ligands are slightly more trans to each other in complex 2. The coordination geometries of Fe-centres reveal that both complexes 1 and 2 possess a distorted trigonal planar geometry as indicated by Σangle of 359.8° and 359.9° respectively and are in agreement with the reported structure (2) .44 The longer C–N bond lengths of 1.343–1.345 Å in complex 1 and 1.397–1.407 Å in complex 2 than that of 1.315(3) Å in free carbone, indicate spin delocalization onto ligands (C\(_{\text{AAC}}\) ← Fe) .44 The dissociation of (cAAC\(_{\text{Me}}\))\(_2\)Fe–N\(_2\) bond \((\text{cAAC}\(_{\text{Me}}\))\(_2\)Fe–N\(_2\) → (cAAC\(_{\text{Me}}\))Fe + N\(_2\)) in complex 1 and 2 is slightly endothermic (\(\Delta G^{\text{298}} = 18.9–29.6 \text{ kcal mol}^{-1}\)) and the energy of dissociation is 30.1–40.2 kcal mol\(^{-1}\) (bond enthalpy) respectively. The electron affinity of 1 is 13.74 kcal mol\(^{-1}\).

We have employed charge and energy density methods like natural bond orbital (NBO), quantum theory of atoms in molecules (QTAIM) and energy decomposition analysis coupled with natural orbitals for chemical valence (EDA-NOCV) methods to study the nature of the Fe–N bond. The Wiberg bond index (WBI) of 0.82 (1), 0.92 (2) for Fe–N bond and 2.53 (1), 2.43 (2) for N–N bond of 1 and 2, respectively (Table 1). The Fe–N and N–N bond orders are consistent with the Fe–N bond of complex 2 suggests the delocalization of one electron-charge upon reduction of 1. The \(\pi\)-SOMO and \(\pi\)-SOMO – 1 of complex 1 represent the two unpaired electrons residing in \(d_x^2\) and \(d_y^2\) orbitals of the triplet state. The \(\pi\)-SOMO – 1 shows \(\pi\)-interaction of \(d_y^2\) orbital of Fe and lone pair on cAAC ligand with \(\pi_x\)-orbital of N\(_2\), while \(\pi\)-SOMO – 2 indicates \(\pi\)-interaction of \(d_y^2\) orbital of Fe with \(\pi_y\)-orbital of N\(_2\) (Fig. S2†). Whereas \(\pi\)-SOMO of complex 2 represents an unpaired electron in \(d_y^2\) orbital of Fe showing small amount of interaction with \(\pi_y\) orbital of N\(_2\). The \(\pi\)-SOMO – 1, \(\pi\)-SOMO – 2 and \(\pi\)-SOMO – 3 indicate the interaction of \(d_{xy}\), \(d_{xz}\), \(d_{yz}\) and \(d_x^2\) orbitals of Fe with \(\pi_y\), \(\pi_z\) and \(\pi_x\) orbital of N\(_2\) (Fig. S3†). The QTAIM analysis shows a bond path (Fig. S4†) and considerable electron density \(\rho(r)\) along the Fe–N bond path in both complexes 1 and 2 (Table 2). Little increase in \(\rho(r)\) along Fe–N and C\(_{\text{AAC}}\)-Fe bond paths in complex 2 corroborates the delocalization of electron density and agrees with the charge distribution from NBO analysis. The ellipticity (\(e_{\text{BCP}} = \lambda_1/\lambda_2 - 1\))

| Bond | \(\rho(r)\) | \(\nabla^2 \rho(r)\) | \(H(r)\) | \(V(r)\) | \(G(r)\) | \(e_{\text{BCP}}\) |
|------|-------------|------------------|--------|--------|--------|---------|
| Fe–N(1) | 0.131 | 0.796 | −0.039 | −0.277 | 0.238 | 0.248 |
| Fe–N(2) | 0.142 | 0.342 | −0.056 | −0.198 | 0.140 | 0.318 |
| Fe–C(1) | 0.139 | 0.793 | −0.046 | −0.290 | 0.244 | 0.383 |
| Fe–C(2) | 0.142 | 0.376 | −0.072 | −0.237 | 0.165 | 0.107 |

Table 2 AIM results of the (cAAC)\(_2\)Fe–N\(_2\) bonds of complex 1 and anionic complex 2 at the BP86-D3(BJ)/def2-TZVPP level of theory. (The values are in a.u.)

| Complex | Bond | ON | Polarization and hybridization (%) | WBI | \(q_{\text{Fe}}\) | \(q_{\text{N}}\) | \(q_{\text{AAC}}\) |
|---------|------|----|----------------------------------|-----|---------|--------|--------|
| 1       | Fe–N | 0.99 | Fe: 19.4 s(21.3), p(19.4), d(59.3) | N: 80.6 s(58.4), p(41.6) | 0.82 | 0.440 | −0.122 | 0.144 |
|         | C–Fe | 0.96 | Fe: 28.5 s(20.0), p(13.8), d(66.2) | C: 71.5 s(41.8), p(58.2) | 0.84 |     |       |       |
|         |      | 0.91 | Fe: 75.3 s(0.0), p(4.7), d(95.8) | C: 24.7 s(0.8), p(99.2) |     |       |       |       |
| 2       | Fe–N | —   | —                               | —   | 0.92 | −0.223 | −0.275 | −0.510 |
|         | C–Fe | 0.97 | Fe: 37.1 s(45.6), p(8.3), d(71.1) | C: 62.9 s(45.3), p(54.7) | 1.09 |     |       |       |
|         |      | 0.90 | Fe: 68.4 s(8.0), p(7.5), d(91.7) | C: 31.6 s(2.0), p(99.8) |     |       |       |       |
|         | (cAAC)\(_2\)Fe | C–Fe | 0.90 | Fe: 14.6 s(42.5), p(50.0), d(7.5) | C: 85.4 s(39.5), p(60.5) | 0.88 | 0.245 | —     | −0.244 |
|         |      | 0.90 | Fe: 98.9 s(0.4), p(0.2), d(99.4) | C: 1.1 s(5.6), p(94.4) |     |       |       |       |

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is a measure of bond order and in general, the $e_{BCP}$ of a single and triple bond is close to zero because of cylindrical contours of electron density $\rho$, while for double bond the value is greater than zero. This is due to the asymmetric distribution of electron density $\rho$ perpendicular to the bond path for a double bond. The ellipticity $\ell$ values of 0.248 and 0.383 for the Fe–N bond of complexes 1 and 2 suggests the possible multiple bond character.

The EDA-NOCV method is more appropriate in explaining the nature of the bond as one of the major strengths of the method is its ability to provide the best bonding model to represent the bonding situation in the electronic geometry. To give the best bonding description of Fe–N bond by EDA-NOCV method, we have considered neutral [(cAACMe)$_2$Fe] fragment in electronic triplet state and neutral N$_2$ fragment in electronic singlet state ($1\Sigma_g^+$) for complex 1 and mono-ionic [(cAACMe)$_2$Fe]$^+$ fragment in electronic doublet state and neutral N$_2$ fragment in electronic singlet state ($1\Sigma_g^+$) for complex 2 (Table 3). The instantaneous interaction ($\Delta E_{\text{inst}}$) demonstrates the strength of the bond and $\Delta E_{\text{int}}$ for Fe$^0$-complex 1 (87.9 kcal mol$^{-1}$) is significantly higher than that of Fe$^{-1}$-complex 2 (63.8 kcal mol$^{-1}$). This lowering of instantaneous interaction is favourable as the reduced Fe$^{-1}$-complex 2 is the active species in the catalytic conversion of N$_2$ into vacant d-type anti-bonding orbital (LUMO) of Fe into vacant degenerate $\pi^*$ orbital LUMO (1$p_z$) of N$_2$ and partly into SOMO (d$_{xz}$) of Fe center and from d$_{xz}$ orbital (HOMO–1) of Fe into vacant degenerate $\pi^*$ orbital LUMO$^*$ (1$p_y$) of N$_2$ in second and third orbital terms respectively. The $\pi$-backdonations together contribute 53.9% to the total orbital interactions (Table 3). The weaker fourth orbital term (4.6%) is due to $\sigma$-electron donation (Fe $\rightarrow$ N$_2$) from HOMO–2 (2$\sigma_g^*$) of N$_2$ into vacant d-type orbital (LUMO) of Fe and the two Fe $\rightarrow$ N$_2$ $\sigma$ electron donations ($\Delta E_{\text{orb1}}, \Delta E_{\text{orb2}}$) together contribute 42.6% (Fig. 2) of 1. Table 3 shows that the Fe$^0$ $\rightarrow$ N$_2$ $\pi$-backdonation ($\Delta E_{\text{orb2}}$) in 1 is nearly 10% higher than $\sigma$-donation ($\Delta E_{\text{orb1}}$). The fluctuations of electron clouds

| Energy | Interaction | (cAAC)$_2$Fe (T) + [N$_2$] (S); 1 | [(cAAC)$_2$Fe$^-$ (D) + [N$_2$] (S); 2 |
|--------|-------------|---------------------------------|----------------------------------|
| $\Delta E_{\text{inst}}$ | | $-87.9$ | $-63.8$ |
| $\Delta E_{\text{pair}}$ | | $190.2$ | $164.1$ |
| $\Delta E_{\text{disp}}$ | | $-5.2$ (1.9%) | $-4.1$ (1.8%) |
| $\Delta E_{\text{elstat}}$ | | $-111.9$ (40.2%) | $-102.4$ (45.0%) |
| $\Delta E_{\text{orb1}}$ | | $-161.0$ (57.9%) | $-121.4$ (53.2%) |
| $\Delta E_{\text{orb2}}$ | | $-61.4$ (38.1%) | $-39.4$ (32.4%) |
| $\Delta E_{\text{orb3}}$ | | $-53.6$ (33.3%) | $-34.0$ (28.0%) |
| $\Delta E_{\text{orb4}}$ | | $-33.2$ (20.6%) | $-25.2$ (20.8%) |
| $\Delta E_{\text{orb4}}$ | | $-7.5$ (4.6%) | $-14.7$ (12.1%) |
| $\Delta E_{\text{orb5}}$ | | $-5.3$ (3.3%) | $-8.1$ (6.7%) |

The values in the parentheses show the contribution to the total attractive interaction $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}}$ \footnote{The values in parentheses show the contribution to the total attractive interaction $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}}$.}
Fig. 2  The shape of the deformation densities $\Delta \rho_{(1-4)}$ that correspond to $\Delta E_{\text{orb}(1-4)}$ and the associated MOs of (cAAC)$_2$Fe–N$_2$ (1) and the fragments orbitals of (cAAC)$_2$Fe in triplet state and N$_2$ in the singlet state at the BP86-D3(BJ)/TZ2P level. Isosurface values of 0.003 au for $\Delta \rho_{(1-4)}$. The eigenvalues $|\nu_i|/|\nu_j|$ give the size of the charge migration in e. The direction of the charge flow of the deformation densities is red $\rightarrow$ blue. Energies are in kcal mol$^{-1}$.
Fig. 3  The shape of the deformation densities $\Delta \rho_{(1)-(4)}$ that correspond to $\Delta E_{\text{orb}(1)-(4)}$ and the associated MOs of $\text{[(cAAC)$_2$Fe(N$_2$)$_2$]$^-$} (2)$ and the fragments orbitals of $\text{[(cAAC)$_2$Fe]$^-$}$ in doublet state and $\text{N}_2$ in the singlet state at the BP86-D3(BJ)/TZ2P level. Isosurface values of 0.003 au for $\Delta \rho_{(1)-(4)}$. The eigenvalues $|\nu|$ give the size of the charge migration in e. The direction of the charge flow of the deformation densities is red $\rightarrow$ blue.

$\Delta \rho_{(1)}$
$\Delta E_{\text{orb}(1)} = -39.4; |\nu_{1\alpha}/\nu_{1\beta}| = 0.42/0.90$

$\Delta \rho_{(2)}$
$\Delta E_{\text{orb}(2)} = -34.0; |\nu_{2\alpha}/\nu_{2\beta}| = 0.37/0.39$

$\Delta \rho_{(3)}$
$\Delta E_{\text{orb}(3)} = -25.2; |\nu_{3\alpha}/\nu_{3\beta}| = 0.29/0.31$

$\Delta \rho_{(4)}$
$\Delta E_{\text{orb}(4)} = -14.7; |\nu_{4\alpha}/\nu_{4\beta}| = 0.11/0.10$
on cAAC ligands during the formation of σ- and π-bonds as expected since cAAC is known as both σ-donor and π-acceptor.46

In contrast, the first three orbital terms (ΔEorb1-3) of complex 2 represent π-electron backdonations (Fe → N2). While the first orbital term (ΔEorb1) comes from the π-electron backdonation from dπ orbital (HOMO) of Fe− to degenerate vacant π(pπ)∗ orbital (LUMO0) of N2, the second orbital term (ΔEorb2) is due to π-backdonation from dπ,y orbital (HOMO-2) into vacant degenerate π* orbital (LUMO) (1πg) of N2. The third orbital term (ΔEorb3) is due to π-backdonation from dπ,z orbital (HOMO−1) of Fe− into vacant degenerate π* orbital LUMO′ (1πg) of N2. The three π-backdonations together contribute 81.2% of the total orbital contributions. The fourth orbital term (ΔEorb4) represents the σ electron donation (Fe ← N2) from HOMO (3σg∗) of N2 into vacant d-type orbital (LUMO) of Fe and contributes 12.1% to the total orbital interactions (Fig. 3). It is to be observed that due to the mixing of orbitals of cAAC ligand, the shapes of d orbitals of Fe are slightly deformed and can be seen from the associated molecular orbitals of [(cAAC)2Fe] fragment in Fig. 2 and 3. The mixing of the pπ-orbital of cAAC ligands with d-orbitals of Fe-centre of 1 is much higher than that of 2.

Overall, Fe → N2 π-backdonations are stronger than Fe ← N2 σ-donations in both complexes 1 and 2. The percentage of Fe → N2 π-backdonation in 2 is nearly one and half times higher than that of 1 and Fe ← N2 σ-donation in 2 is over nearly four times lower than that of 1. A close look at the deformation densities (Fig. 2 and 3) in 1–2 suggests that electronic effect of cAAC ligands is much lower in 2 than in 1 during the formations of σ- and π-bonds. The matrix isolated triplet M(N2)8 (M = Ca, Sr, Ba) species are also mainly stabilized by [M(dπ)] → (N2)8 σ-backdonation.47 The EDA-NOCV results, in particular, the σ-donation and π-backdonations and the ellipticity values of QTAIM agrees well with each other and ascertain the speculation of the authors that “the ability of [(CAAC)2Fe]/[(CAAC)2Fe(N2)] to perform nitrogen fixation may arise from the relative flexibility of the system, which is capable of switching between two- and three-coordinate geometries, and allows the formation of highly covalent Fe–N2 multiple-bond interactions”.48

In conclusion, although a plethora of iron complexes are shown to bind N2 molecules in past. The nature of the bonding interactions between Fe-centre and N2 molecule has not been studied by EDA-NOCV. This study for the first time has provided a quantitative and detailed illustration orbital interactions to shed light on the engrossing Fe–N2 bond. The bonding interactions between (L)2Fe n (n = 0, −1) and N2 fragments of two low coordinate and low valence Fe-complexes have been studied by DFT, NBO, QTAIM and EDA-NOCV analyses which revealed that Fe → N2 π-backdonations are major interactions for efficient N2 binding. However, the N2 → Fe σ-donation contributions is not negligible in both the complexes. Fe6° center of (L)2Fe6° of 1 is a better σ-acceptor than Fe−1 of 2 while Fe−1 center of (L)2Fe−1 of 2 is a much stronger π-backdonor due to its richness of electron densities in the latter. The Fe–N2 interaction energy of 1 is significantly higher than that of 2. These two Fe-complexes are an unprecedented set of complexes among the N2-bonded Fe-complexes which have been studied by EDA-NOCV calculations. The role of cAAC has been clearly shown by the deformation densities during N2 binding at Fe-centre (charge flow from red → blue). Our EDA-NOCV analysis will help the synthetic chemists to have much clearer view/understanding on the bonding interactions of capturing Fe–N2 bond and design a superior metal-complex for efficient N2 binding in their future studies.

**Computational methods**

Geometry optimizations and vibrational frequencies calculations of (cAAC)2Fe–N2 as neutral (1) and anionic complexes (2) in singlet, doublet, triplet and quintet electronic states has been carried out at the BP86-D3(BJ)/Def2TZVPP, for triplet and doublet states additionally at the TPSS-D3(BJ)/Def2TZVPP and PW6B95-D3/Def2TZVPP level in gas phase. The absence of imaginary frequencies assures the minima on potential energy surface. We have also optimized complex 1 in diethyl ether solvent using PCM solvation model.49 All the calculations have been performed using Gaussian 16 program package.50 NBO calculations have been performed using NBO 6.0 (ref. 52) program to evaluate partial charges, Wiberg bond indices (WBI)33 and natural bond orbitals. The nature of Fe–N2 bonds in complexes 1 and 2 were analyzed by energy decomposition analysis (EDA)44 coupled with natural orbital for chemical valence (NOCV)50 using ADF 2018.105 program package.46 EDA-NOCV calculations were carried out at the BP86-D3(BJ)/TZ2P57 level using the geometries optimized at BP86-D3(BJ)/def2-TZVPP level. EDA-NOCV method involves the decomposition of the intrinsinc interaction energy (ΔEint) between two fragments into four energy components as follows:

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}}.$$  

where the electrostatic ΔEelstat term is originated from the quasi-classical electrostatic interaction between the unperturbed charge distributions of the prepared fragments, the Pauli repulsion ΔEPauli is the energy change associated with the transformation from the superposition of the unperturbed electron densities of the isolated fragments to the wavefunction, which properly obeys the Pauli principle through explicit anti-symmetrisation and renormalization of the production of the wavefunction. Dispersion interaction, ΔEdisp is also obtained as we used D3(BJ). The orbital term ΔEorb comes from the mixing of orbitals, charge transfer and polarization between the isolated fragments. This can be further divided into contributions from each irreducible representation of the point group of the interacting system as follows:

$$\Delta E_{\text{orb}} = \sum_r \Delta E_r.$$  

The combined EDA-NOCV method is able to partition the total orbital interactions into pairwise contributions of the orbital interactions which is important in providing a complete picture of the bonding. The charge deformation Δρ(r), which comes from the mixing of the orbital pairs ψi(r) and ψj(r) of the
interacting fragments, gives the magnitude and the shape of the charge flow due to the orbital interactions (eqn (3)), and the associated orbital energy $\Delta E_{\text{orb}}$ presents the amount of orbital energy coming from such interaction (eqn (4)).

\[
\Delta \rho_{\text{orb}}(r) = \sum_{k} \Delta \rho_{k}(r) = \sum_{k} \sum_{l=1}^{N/2} \rho_{k}(r) [-\psi_{k,-2}(r) + \psi_{k,2}(r)]
\]

(3)

\[
\Delta E_{\text{orb}} = \sum_{k} \Delta E_{\text{orb}}^{(k)} = \sum_{k} \rho_{k} \left[ -F_{k,-2}^{\text{TS}} + F_{k,2}^{\text{TS}} \right]
\]

(4)

Readers are further referred to the recent reviews articles to know more about the EDA-NOCV method and its applications.\(^\ast\)

**Conflicts of interest**

Authors do not have any conflict of interest.

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