Coordination of N₂ ligands to lanthanum: the complexes La (N₂)_{1–8}

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Abstract

The structures and bonding properties of La(N₂)_x ($x = 1–8$) complexes were investigated by density functional theory (DFT) computations using the B3LYP exchange-correlation functional in conjunction with a quasi-relativistic pseudopotential for La. The quality of the DFT electronic structures was confirmed in selected cases by relativistic multireference calculations using CASPT2 theory. From the end-on and side-on dinitrogen coordination modes in general, the structures with end-on coordination were found to be the more stable. The first coordination sphere of the complexes is filled by eight and six N₂ ligands in the end-on and side-on type species, respectively. The main bonding interaction is the donation of La 5d valence electrons to anti-bonding orbitals of N₂ resulting in characteristic elongation of the NN bonds. These directional interactions determine the (from steric point of view in several cases less logic) equilibrium molecular structures. The charge transfer resulted in partial charges up to 1.5 e of the originally neutral components (La, N₂) leading to electrostatic attractive interactions which compose the minor contribution in the bonding.

Keywords Lanthanum · Dinitrogen complex · Structure · Bonding · DFT · Multireference calculations

Introduction

Since the discovery of the Haber-Bosch process in 1909, considerable efforts are focused on the basic understanding of nitrogen fixation. This operation is achieved by chemisorption of N₂ on a metal catalyst's surface, where the unsaturated valence shell of the metal establishes charge transfer interactions with the relatively inert N₂ molecule. An important step in this research was the discovery of the first ruthenium dinitrogen complexes in the 1960s and since then strenuous efforts were made on the synthesis of transition metal dinitrogen complexes [1, 2]. Particular attention was paid on coordinatively unsaturated complexes involved in the catalytic reduction of N₂ [3–7].

In general, coordinatively unsaturated metal dinitrogen complexes of metals have low stability and thus can be

synthesised, isolated and studied only under extreme conditions. The most efficient tool in this research proved to be the matrix-isolation technique, combined initially with vibrational and electronic spectroscopy. Examples on transition metal complexes include the matrix-isolation IR study of FeN₂ [8], Ni(N₂)_x ($x = 1–4$) [9–14], Pd(N₂)_x ($x = 1–3$) [10] and Pt(N₂)_x ($x = 1–3$) [11]. Support for the proposed structures and bonding properties were provided by, over the years increasingly sophisticated, quantum chemical calculations, e.g. FeN₂ [15], Ni(N₂)_x ($x = 1–4$) [12, 14, 16–18] and WN_x ($x = 1–9$) [19]. Related studies with rare earth elements include the co-deposition of the laser-ablated metals and N₂ gas in cryogenic matrices with a posteriori investigations by matrix-isolation IR spectroscopy [20–23]. Relevant compounds include various organometallic lanthanide dinitrogen complexes with fully characterised examples for the entire series of lanthanides [24–27].

Dinitrogen complexes of metals can exhibit different binding geometries of N₂: end-on terminal, end-on bridging between two metals, side-on terminal, side-on bridging and side-on end-on bridging. They were theoretically investigated by DFT calculations on transition metal complexes [28].

In contrast to the extended theoretical studies on transition metal complexes [12, 14–19, 28], for the rare earth dinitrogen Ln(N₂)_x species, only three theoretical reports were found in the literature.

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Very recently, Zhao et al. studied the whole lanthanide series of $\text{Ln}(\text{N}_2)$ molecules using the mPW3PBE hybrid exchange-correlation functional in conjunction with quasi-relativistic 4f-in-valence pseudopotentials for the lanthanides and 6-31G* basis set for nitrogen [29]. The covered molecular properties were the geometries, HOMO-LUMO energy gaps, and magnetic and electronic properties. These calculations predicted the end-on $^4\text{La}(\text{N}_2)$ structure to be favoured by 47 kJ/mol over $^2\text{La}(\text{N}_2)$ with a side-on structure. From the bonding properties, the π -type HOMO orbital and the atomic charges were presented.

Teng and Xu performed DFT calculations using the BP86 and B3LYP functionals in order to assist the interpretation of the matrix-isolation IR spectra of the reaction products formed by laser-ablated La co-deposited with N_2 [23]. In the spectra, several species were identified and their electronic structures, dissociation energies and vibrational data were reported. On the basis of isotope experiments and computed data, the authors concluded on the dominant presence of end-on $^4\text{La}(\text{N}_2)$ in the argon matrix.

The only theoretical study on complexes of a lanthanide atom with more than one N_2 ligands is an early SCF/3-21G computational study of holmium complexes by Ermilov et al. [30] using a 4f-in-valence pseudopotential [31] for Ho. Beyond the low-quality computational level, this study has also other limitations: only quartet spin multiplicity and complexes up to six N_2 ligands were considered. However, the small energy difference between the quartet and sextet Ho [32] may readily be overcompensated by N_2 bonding, particularly in the larger complexes. Therefore, the sextet $\text{Ho}(\text{N}_2)_x$ species should not be neglected. (Note that Zhao et al., in contrast, studied only the sextet HoN_2 [29].) Most striking is, however, the instability of HoN_2 at the SCF/3-21G level: in contrast to chemical intuition, the computations predicted dissociation to $\text{HoN} + \text{N}$ [30].

The goal of our ongoing research is the elucidation of structural, energetic and spectroscopic properties of $\text{Ln}(\text{N}_2)_x$ complexes by state of the art quantum chemical calculations. In the present work, the results on lanthanum complexes are reported, which metal is the prototype of the rare earth elements.

The neutral lanthanum atom has an open-shell $[\text{Xe}]4f^05d^16s^2$ electronic structure with three valence electrons. The ground electronic state is a doublet ($^2\text{D}_{3/2}$) [32], in which the single 5d electron (in contrast to the filled $6s^2$ subshell) is suited for electron-sharing interactions. The first quartet state ($^4\text{F}_{3/2}$) lies higher in energy by 2668 cm^{-1} and has an electron configuration of $[\text{Xe}]4f^05d^26s^1$ [32]. Here, the two singly occupied 5d orbitals can facilitate two orbital overlapping interactions in contrast to the single interaction by the doublet ground state.

Description of the results will start with the analysis of the end-on complexes, because literature data on complexes of transition and rare earth metals with N_2 show generally the preference of this structure [12, 14–18, 23–28]. Subsequently,

the related side-on isomers will be discussed and compared with the end-on isomers.

Computational details

The DFT computations have been performed with the Gaussian09 suit of programs [33] using the B3LYP [34, 35] exchange-correlation functional in conjunction with the quasi-relativistic small-core 4f-in-valence pseudopotential [36]. The valence basis set treating the $4s4p4d4f5s5p5d6s$ orbitals had the contraction scheme of $[14s13p10d8f6g]/[10s8p5d4f3g]$ [37]. For nitrogen, the correlation-consistent cc-pVTZ basis set [38] was applied. In order to account for dispersion interaction in the model (particularly the large) structures, the B3LYP functional has been extended with the D3 version of Grimme's dispersion correction using the original D3 damping function (D3) [39].

The computed model structures are neutral. Doublet and quartet spin multiplicities have been probed according to the number of expected unpaired electrons. In most cases, these different electronic structures resulted in different spatial structures. The minimum character of the obtained stationary points on the potential energy surface has been confirmed in all cases by frequency analysis. The unpaired electrons in the model structures required spin unrestricted calculations. The spin contamination was checked in all cases and for the quartets, always the theoretical value of 3.75 was found. For the doublets, mostly the theoretical value of 0.75 was obtained, in a few cases deviating up to 0.78.

The atomic charges and orbital populations were assessed using the natural bond orbital (NBO) model [40] by means of the NBO 6.0 code [41, 42].

In order to assess the reliability of the electronic structures predicted by B3LYP, single-point relativistic multireference calculations were performed on selected $\text{La}(\text{N}_2)_x$ species on their B3LYP optimised geometries. The properties in focus included the character of the main electron configuration (whether it agrees with the electronic properties from the B3LYP calculations), its contribution (%) in the multi-determinant wavefunction and the relative energies of the doublet and quartet states.

The complete active space self-consistent field (CASSCF) method [43] has been used to generate molecular orbitals and reference functions for subsequent multiconfigurational second-order perturbation theory calculations of the dynamic correlation energy (CASPT2) [44, 45] with frozen 1 s for N, and up to 3d for La.

In the CASSCF calculations, the scalar relativistic effects were taken into account using the second-order Douglas-Kroll-Hess Hamiltonian [46, 47]. The all electron basis sets of atomic natural orbital type, developed for relativistic calculations (ANO-RCC) with the Douglas-Kroll-Hess Hamiltonian [46, 47], had contraction schemes of $24s21p15d5f3g2h.8s7p5d2f1g$ [48] and

14s9p4d3f2g.4s3p2d1f [49] for La and N, respectively, corresponding to triple-zeta valence plus polarisation (TZP) quality. In the treatment of two-electron integrals, the Cholesky decomposition method [50] was applied.

The active space has been constructed on the basis of state-averaged test calculations using 5 roots. Based on the observed occupations [51] and cost considerations in case of the larger model structures, the following active spaces (electron/orbital) were applied in the calculations of the various structures: 7/10 for $\text{La}(\text{N}_2)$ while 11/12 for $\text{La}(\text{N}_2)_2$ and $\text{La}(\text{N}_2)_6$. For these CASPT2 calculations, the MOLCAS 8.2 code [52, 53] was applied.

In general, the electronic structures from the B3LYP calculations were confirmed by CASPT2. The dominant electron configurations in the CAS were >85% and >70% for the quartets and doublets, respectively. The minor contributions in the multi-determinant wavefunction appeared only by a few percent, suggesting that the title molecular systems can be reasonably modelled by DFT. This refers particularly to the structure and bonding interactions. On the other hand, the mostly very small energy differences between the doublet and quartet forms should be treated with caution.

Results and discussion

Geometry and bonding of end-on structures

A compilation of the end-on structures is shown in Fig. 1 while the bond distances and selected bond angles are given in Table 1.

In case of the small $\text{La}(\text{N}_2)_x$ complexes ($x = 1\text{--}4$), the doublet and quartet states have very similar structures with somewhat different bond distances and angles. As the complexes are formed from neutral La atom and N_2 molecules, the arrangements of the N_2 ligands around La are governed by orbital interactions. These are donor-acceptor interactions facilitated by the low-lying empty valence atomic orbitals (primarily 5d) of La and anti-bonding orbitals of N_2 . Therefore, both $\text{N}_2 \rightarrow \text{La}$ (ligand-to-metal donation) and $\text{La} \rightarrow \text{N}_2$ (metal-to-ligand back donation) charge transfers might be possible in these complexes. The charge transfer processes are governed by the spatial arrangements of the interacting donor and acceptor orbitals. They differ in the various complexes due to the different number of ligands and different spatial structures. In addition, they depend also on the (doublet or quartet) spin state of La, as it defines the population of the valence La orbitals.

Both the doublet and quartet $\text{La}(\text{N}_2)$ complexes have a linear structure. The La– N_2 bond distances of 2.4 and 2.3 Å, respectively, are somewhat smaller than the sum of single-bond covalent radii of La (1.80 Å) and N (0.71 Å) [54]. The NN bond distances of around 1.13 Å in the two complexes are

between the NN triple and double-bond lengths of 1.08 Å and 1.20 Å, respectively, derived from the known triple- and double-bond radii of N (0.54 and 0.60 Å, respectively [55]). Hence, the geometrical parameters suggest a near single-bond character of the $\text{La} \dots \text{N}_2$ interaction, while a considerably weakened triple NN bond. It is noteworthy that the present $^4\text{La-N}_2$ bond distance deviates by 0.04 Å from that obtained with the mPW3PBE functional by Zhao et al. [29]. The deviation from the BP86 and B3LYP results of Teng and Xu [23] is of similar magnitude. The shorter B3LYP $^4\text{La-N}_2$ bond distance from the latter study is probably due to their smaller basis set.

Regarding the relative stabilities of doublet and quartet $\text{La}(\text{N}_2)$, the present B3LYP (similarly to previous DFT [23]) calculations predicted the quartet state to be more stable than the doublet one by ca. 6 kJ/mol, while the CASPT2 computations favoured the doublet state by a similar magnitude (cf. Table 1). This small energy difference, however, is within the uncertainties of the applied computational levels. Therefore, they alone are not suitable to draw unambiguous conclusion on the ground state of $\text{La}(\text{N}_2)$. The known doublet ground state of the La atom [32] is not determinative in this case either, because orbital interactions can readily stabilise low-lying excited states.

The favoured stability of quartet $\text{La}(\text{N}_2)$ as predicted by DFT is supported by matrix-isolation IR data [23]. In the spectrum of the reaction products of laser-ablated La and N_2 gas (deposited in Ar matrix), an absorption band at 1749.8 cm^{-1} has been reported and assigned to NN stretching of end-on $^4\text{La}(\text{N}_2)$. Note that the B3LYP functional tends to overestimate this vibrational frequency (see ref. [23] and the present 1889-cm^{-1} value in the Supplementary Information) while BP86 provided a better performance [23]. In another related studies, the absorption bands in this range of the matrix-isolation IR spectra seem to be erroneously attributed to side-on $\text{Ln}(\text{N}_2)$ species [20–22]. The more extensive donor-acceptor interactions in the η^2 -coordinated side-on $\text{Ln}(\text{N}_2)$ result in a larger elongation of the NN bond (vide supra); therefore, lower NN vibrational frequencies are expected.

The donor-acceptor interactions in end-on $\text{La}(\text{N}_2)_x$ are analysed on the basis of characteristic molecular orbitals and natural atomic charges shown in Figs. 2 and 3 and Table 2, respectively. Table 2 includes also the populations of the La valence orbitals.

The La– N_2 bond is established jointly by donor-acceptor and electrostatic interactions. In the view that the complexes are formed from neutral components, the former interaction is likely the major one. Analysis of the molecular orbitals revealed a π -type bonding interaction between the 5d π orbitals of La and the 2p orbitals of the adjacent N atoms (cf. Fig. 2). The overlap of these π -type orbitals is most efficient in a linear La–NN arrangement, which explains the linear structure. The shapes of the orbitals over the N_2 moiety correspond to anti-

Fig. 1 Structures of end-on $\text{La}(\text{N}_2)_x$ complexes optimised by B3LYP calculations

bonding orbitals. Hence, the found bonding molecular orbitals describe $\text{La} \rightarrow \text{N}_2$ charge transfer. Molecular orbitals corresponding to $\text{N}_2 \rightarrow \text{La}$ charge transfer could not be found either among the B3LYP or the CASSCF orbitals. Accordingly, a ligand-to-metal donation does not seem to be characteristic for the end-on $\text{La}(\text{N}_2)$ complexes. The B3LYP and multireference CASPT2 calculations agree in the above described bonding scenarios, supporting the reliability of B3LYP molecular properties. Note that similar bonding situation was reported in the $\text{Ni}(\text{N}_2)_2$ complex with $3d_8$ donor orbitals of Ni [14]. The different spatial forms of the La and Ni donor orbitals can be responsible for some structural differences found in their larger complexes (vide infra).

The main difference in the bonding between the doublet and quartet $\text{La}(\text{N}_2)$ is that in the doublet species, there is only one $5d\pi-2p$ orbital overlap formed by the single unpaired $5d_8$

electron of La, while in the quartet, two orthogonal $5d\pi-2p$ orbital overlaps appear, formed by both unpaired $5d_8$ electrons of La. The remaining valence electrons of the two species form non-bonding (lone pair and lone electron, respectively) molecular orbitals.

The consequence of the $\text{La} \rightarrow \text{N}_2$ charge transfer is the partial positive charge of La and a negative one of the N_2 ligand (cf. Table 2). This facilitates an electrostatic attraction contribution to the bonding.

The different number of one-electron bonding orbitals in the two electronic states results in characteristic differences in the molecular parameters. The atomic charge of La is larger in quartet $\text{La}(\text{N}_2)$ due to the transferred larger charge to the N_2 anti-bonding orbital (cf. Table 2). The geometrical consequence of the latter interaction is the NN bond distance lengthened more in the quartet than in the doublet species (Table 1)

Table 1 Relative energies and selected bond distances of the end-on type $\text{La}(\text{N}_2)_x$ complexes from B3LYP calculations

$\text{La}(\text{N}_2)_x$	Spin	Sym	ΔE	La-N ₂	NN
$\text{La}(\text{N}_2)$	2	$C_{\infty v}$	5.8 ^a	2.406	1.123
	4	$C_{\infty v}$	0.0 ^a	2.303	1.138
$\text{La}(\text{N}_2)_2$	2	$D_{\infty h}$	11.5 ^b	2.479 (2)	1.119 (2)
	4	$D_{\infty h}$	0.0	2.487 (2)	1.118 (2)
$\text{La}(\text{N}_2)_3$	2	C_1	16.5	2.422 ... 2.464	1.118 ... 1.125
	4	C_{3v}	0.0	2.434 (3)	1.123 (3)
$\text{La}(\text{N}_2)_4$	2	C_{2v}	14.3	2.546 (2) ^c , 2.469 (2) ^d	1.115 (2) ^c , 1.118 (2) ^d
	4	C_{2v}	0.0	2.560 (2) ^c , 2.462 (2) ^d	1.113 (2) ^c , 1.118 (2) ^d
$\text{La}(\text{N}_2)_5$	2	C_s	20.6	2.545 ... 2.571	1.110 ... 1.114
	4	C_{4v}	0.0	2.580 (4) ^d , 2.488 ^c	1.110 (4) ^d , 1.115 ^c
$\text{La}(\text{N}_2)_6$	2	D_{4h}	11.9 ^c	2.599 (4) ^d , 2.590 (2) ^c	1.108 (4) ^d , 1.109 (2) ^c
	4	O_h	0.0	2.598 (6)	1.108 (6)
$\text{La}(\text{N}_2)_7$	2	C_s	–	2.599 ... 2.627	1.106
$\text{La}(\text{N}_2)_8$	2	D_{4h}	0.0	2.645 (8)	1.104 (8)
	4	D_{4d}	63.9	2.656 (8)	1.107 (8)

Relative energies are given in kJ/mol, bond distances in angstroms. In symmetric structures, the multiplicities are given in parentheses

^a The CASPT2 calculations predicted the doublet $\text{La}(\text{N}_2)$ being more stable by 4.9 kJ/mol than the quartet one

^b At the CASPT2 level, the energy difference is 32.7 kJ/mol (for the favour of the quartet)

^c Axial position, see Fig. 1

^d Equatorial position, see Fig. 1

^e At the CASPT2 level, the energy difference is 45.4 kJ/mol (for the favour of the quartet)

with respect to the NN bond of the free N_2 molecule (1.091 Å, calculated at the applied B3LYP level). Accordingly, the stronger quartet La-N₂ bond is shorter by 0.1 Å than that in doublet $\text{La}(\text{N}_2)$.

Similar charge transfer interactions appear in $\text{La}(\text{N}_2)_2$, where both the doublet and quartet La atoms establish two orthogonal orbital overlaps with the N_2 moieties (Fig. 2). For that, one of the two 6s electrons of the doublet La state needs to be promoted (with preserved spin) to a 5d_s orbital; thus, the electron configuration of La in $\text{La}(\text{N}_2)_2$ is 5d²6s¹. Accordingly, the calculations indicate two orthogonal one-electron three-centre donor-acceptor bonds and a lone non-bonding electron on La. Due to the identical bonding scenario, the bond distances of the doublet and quartet $\text{La}(\text{N}_2)_2$ are nearly the same and slightly longer than in quartet $\text{La}(\text{N}_2)$.

The non-bonding La 6s electrons present in $\text{La}(\text{N}_2)$ and $\text{La}(\text{N}_2)_2$ are not retained in the larger complexes. The larger number of ligands ($x = 3-8$) require additional orbitals getting involved in the bonding; therefore, the electron configuration of La in these complexes is 5d³6s⁰. In all of these complexes, three (in most cases) delocalised one-electron π -type bonding orbitals were found. Examples are shown in Fig. 3.

While the linear structures of $\text{La}(\text{N}_2)$ and $\text{La}(\text{N}_2)_2$ agree with those of the Ni analogues [12, 14, 17, 18], the presently obtained structures of $\text{La}(\text{N}_2)_3$ and $\text{La}(\text{N}_2)_4$ differ from the planar D_{3h} and tetrahedral T_d structures of $\text{Ni}(\text{N}_2)_3$ and $\text{Ni}(\text{N}_2)_4$, respectively [18]. The pyramidal $\text{La}(\text{N}_2)_3$ structure

of both spin multiplicities (Fig. 1) is stabilised by more-or-less balanced delocalised bonding orbitals. This balanced delocalisation results in close La-N₂ bond distances in both the doublet and quartet $\text{La}(\text{N}_2)_3$ (cf. Table 1).

In the C_{2v} $\text{La}(\text{N}_2)_4$ structures, the considerable 0.1-Å difference between the axial and equatorial La-N₂ bond distances (Table 1) can be explained by the characteristically different orbital interactions. The shorter axial bonds are formed by two orthogonal, over the vertical N-La-N moiety delocalised bonding orbitals, while the equatorial N_2 ligands are connected to La by a single delocalised bonding orbital only (cf. Fig. 3).

Fig. 2 Characteristic bonding orbitals of end-on $\text{La}(\text{N}_2)_x$ ($x = 1, 2$) complexes

Fig. 3 Selected bonding orbitals of end-on $\text{La}(\text{N}_2)_x$ ($x = 3–8$) complexes

The bonding in the tetragonal pyramid (C_{4v}) $^4\text{La}(\text{N}_2)_5$ has some resemblance to that in $\text{La}(\text{N}_2)_4$: the shorter axial $\text{La}-\text{N}_2$ bond is formed by two orthogonal three-centre orbitals, while the longer equatorial bonds are established by a single five-centre bonding orbital (cf. Fig. 3). The consequence is again a 0.1-Å difference between the axial and equatorial $\text{La}-\text{N}_2$ bond distances. In contrast, the $\text{La}-\text{N}_2$ bond distances of $^2\text{La}(\text{N}_2)_5$ vary in a small range (cf. Table 1) as a result of considerably balanced delocalised bonding orbitals. The different bonding scenario results in a quite high energy difference (20 kJ/mol, cf. Table 1) between the characteristically different structures of the doublet and quartet $\text{La}(\text{N}_2)_5$ species.

For the quartet $\text{La}(\text{N}_2)_6$, the B3LYP computations predicted a highly symmetric octahedral (O_h) structure. The bonding is established by three equivalent (over LaN_4 moieties delocalised) orthogonal molecular orbitals; an example is

shown in Fig. 3. The doublet $\text{La}(\text{N}_2)_6$ is slightly distorted from O_h to D_{4h} symmetry, but the bonding scenario is analogous.

Interestingly, a stable $\text{La}(\text{N}_2)_7$ structure was found for the doublet state only; it has C_s symmetry (Fig. 1). Quartet $\text{La}(\text{N}_2)_7$ seems to be unstable: the geometry optimisations starting from several reasonable initial structures converged to an $\text{La}(\text{N}_2)_6 \cdot \text{N}_2$ adduct in which one N_2 moiety is too far from La for any bonding interaction.

Highly symmetric structures were obtained for the doublet (D_{4h}) and quartet (D_{4d}) $\text{La}(\text{N}_2)_8$. The equivalent $\text{La}-\text{N}_2$ bond distances imply highly delocalised symmetric bonding orbitals in both structures. The one, established by the $5d\sigma$ La orbital positioned in the C_4 rotational axis, is delocalised over all the eight $\text{La}-\text{N}_2$ bonds (cf. Fig. 3). This orbital is common in both the doublet and quartet states. The other two bonding orbitals, however, are characteristically different in the two

Table 2 Selected NBO atomic charges and population of La valence orbitals in the end-on $\text{La}(\text{N}_2)_x$ complexes from B3LYP calculations

$\text{La}(\text{N}_2)_x$	Spin	q_{La}	q_{N}	$q_{\text{N}'}$	$n(6s)$	$n(5d)$	$n(4f)$
$\text{La}(\text{N}_2)$	2	+ 0.37	− 0.37	0.00	1.48	1.09	0.05
	4	+ 0.55	− 0.47	− 0.08	0.93	1.47	0.03
$\text{La}(\text{N}_2)_2$	2	+ 0.64	− 0.31	− 0.01	0.83	1.51	0.02
	4	+ 0.61	− 0.30	− 0.01	0.84	1.52	0.02
$\text{La}(\text{N}_2)_3$	2	+ 0.94	− 0.26 ... − 0.31	− 0.01 ... − 0.03	0.19	1.82	0.05
	4	+ 0.96	− 0.29	− 0.03	0.07	1.92	0.05
$\text{La}(\text{N}_2)_4$	2	+ 0.95	− 0.24	0.0	0.10	1.89	0.05
	4	+ 0.92	− 0.22 ... − 0.24	− 0.01	0.10	1.93	0.04
$\text{La}(\text{N}_2)_5$	2	+ 0.92	− 0.18 ... − 0.22	+ 0.01 ... − 0.02	0.16	1.84	0.06
	4	+ 0.82	− 0.18 ... − 0.20	+ 0.02	0.13	1.99	0.04
$\text{La}(\text{N}_2)_6$	2	+ 0.72	− 0.15	+ 0.03	0.17	2.04	0.04
	4	+ 0.69	− 0.15	+ 0.03	0.17	2.07	0.04
$\text{La}(\text{N}_2)_7$	2	+ 0.59	− 0.11 ... − 0.12	+ 0.03	0.20	2.12	0.06
$\text{La}(\text{N}_2)_8$	2	+ 0.41	− 0.09	+ 0.04	0.23	2.25	0.07
	4	+ 0.69	− 0.12	+ 0.04	0.23	1.82	0.21

Natural atomic charges and orbital populations are given in atomic units (e). N means the nitrogen atom in contact with La

states. In $^2\text{La}(\text{N}_2)_8$, both orbitals are delocalised over all the eight La-N₂ bonds, while in $^4\text{La}(\text{N}_2)_8$, the delocalisation occurs only either in the upper or in the bottom part of the molecule, hence over four La-N₂ bonds only (cf. Fig. 3).

The formation of larger $\text{La}(\text{N}_2)_x$ ($x > 8$) complexes is unlikely due to the steric crowding around La. Indeed, probing $\text{La}(\text{N}_2)_9$, the ninth N₂ ligand escaped from the first coordination sphere of La during geometry optimisation.

The above introduced $\text{La}(\text{N}_2)_x$ structures can be compared with the theoretical structures of $\text{Ho}(\text{N}_2)_{1-6}$ complexes obtained in simple SCF/3-21G calculations by Ermilov et al. [30]. The unreasonable $\text{HoN} \dots \text{N}$ result was already noted in the “Introduction” section (vide supra). Other significant differences appear in the structure of quartet $\text{Ho}(\text{N}_2)_3$ and $\text{La}(\text{N}_2)_3$: the former was predicted to be planar (D_{3h}) in ref. [30] while pyramidal (C_{3v}) by the present calculations. Similarly, the C_{4v} $\text{Ho}(\text{N}_2)_4$ structure is in disagreement with the strongly bent $\text{La}(\text{N}_2)_4$ possessing C_{2v} symmetry. On the other hand, the D_{4h} $\text{Ho}(\text{N}_2)_6$ is quite close to the O_h $\text{La}(\text{N}_2)_6$ structure. On the basis of the expected marginal effect of the partly filled Ho 4f subshell on the bonding interactions, the described differences are likely due to the different theoretical levels and/or to the smaller size of the Ho atom.

An overview of the data in Tables 1 and 2 does reveal some characteristic trends in the molecular parameters of the $\text{La}(\text{N}_2)_x$ species:

1. The La-N₂ bond distances are increased gradually with the increase of x (cf. Table 1). The difference between the largest and smallest La-N₂ bonds is 0.35 Å. This large change can be understood by both the distribution of the

La bonding electron densities among more N₂ ligands and the increasing steric interactions with increasing x .

2. The NN bond distance shows an opposite (decreasing) trend with increasing x , though up to only 0.03 Å due to the rigidity of the triple bond. The shortening of the NN bonds correlates well with increasing NN stretching frequencies (cf. Supplementary Information).
3. The correlation of the two bond distances reflects the geometrical consequences of the charge transfer interactions in $\text{La}(\text{N}_2)_x$: a stronger La-N₂ bond means larger charge transfer to the N₂ anti-bonding orbital, weakening in this way the NN bond. Altogether, the computed bond distances support a considerably weakened NN triple bond in the small complexes, while only a slightly weakened one in the larger ($x \geq 6$) species.

In Table 2, some interesting features can be observed in the atomic charge data. First of all, the atomic charge of La is positive in all the complexes. This is the consequence of the $\text{La} \rightarrow \text{N}_2$ charge transfer decreasing the electron density around La. The variation of the La charge shows a convex curve with a maximum around $x = 3$. In $\text{La}(\text{N}_2)_8$, the charge drops nearly to the value of $\text{La}(\text{N}_2)$. In contrast, the magnitude of the negative charge of the attached N decreases gradually from $x = 1$ to 8. The charge of N' is considerably smaller and has values between − 0.08 and + 0.04 e. These data refer to notable ionic interactions between La and N₂ in the smaller complexes which, however, weaken in the larger species.

The shown orbital (charge transfer) interactions are established by the valence electrons of La. The La valence orbital populations in the two spin states of $\text{La}(\text{N}_2)$ resemble

the different populations in doublet and quartet La atom, respectively. In contrast, in the larger complexes, the La populations in the doublet and quartet $\text{La}(\text{N}_2)_x$ pairs are quite similar. Characteristic is the above-mentioned redistribution of the 6s electron density to the 5d orbitals with increasing size of the complexes. From $\text{La}(\text{N}_2)_3$ on the population of the 6s orbital is between 0.1 and 0.2 e, while that of the 5d orbital is around 2 e. This is undoubtedly due to the spatial suitability of the 5d orbitals for simultaneous overlaps with the orbitals of more than one N_2 ligands. The 4f orbitals are marginally populated—except for the quartet $\text{La}(\text{N}_2)_8$, where the spatial arrangement of the N_2 ligands may require a pronounced hybridisation.

Energetics of end-on structures

Table 3 shows the energies of formation (in terms of ΔH_0 , ΔH_{298} and ΔG_{298}) corresponding to the reactions $\text{La}(\text{N}_2)_{x-1} + \text{N}_2 = \text{La}(\text{N}_2)_x$. They were evaluated from the computed absolute energies corrected for unscaled zero-point vibration (ΔH_0), as well as from enthalpies and Gibbs free energies at 298.15 K and 1 atm (ΔH_{298} and ΔG_{298} , respectively) obtained on the basis of the ideal gas model. The latter data do not include thermal corrections for the electronic energy. Because of the change of species number in the reaction, the molar work term $\Delta(pV) = \Delta nRT$ ($\Delta n = -1$) was also considered.

At 0 K, all reactions are exothermic indicating the favoured formation of the complexes up to $\text{La}(\text{N}_2)_8$. Note that even the largest $\text{La}(\text{N}_2)_8$ complex has a substantial stability with respect to the smaller complexes. The stability trend is approximately linear up to $x=6$. The trend is broken at $\text{La}(\text{N}_2)_7$, which complex has a considerably smaller formation energy as another indication of the less favoured sevenfold

coordination of N_2 ligands around La. This can be due both to the unfavourable directionality of the valence La orbitals for the required orbital interactions and to the increased steric repulsion with respect to the smaller complexes. The latter steric interactions may be responsible for the somewhat smaller formation energy of $\text{La}(\text{N}_2)_8$ too.

The thermal contributions at 298 K increase somewhat the magnitudes of the reaction energies (see ΔH_{298} values in Table 3). In contrast, the entropy effect introduced in the ΔG data decreases them considerably, particularly those of the larger complexes. Upon this latter effect, the formation of $\text{La}(\text{N}_2)_7$ becomes endotherm.

Properties of side-on structures

In the side-on $\text{La}(\text{N}_2)_x$ complexes, the La atom interacts with both N atoms of the N_2 ligands. The optimised structures of these complexes are depicted in Fig. 4 while selected molecular data are given in Table 4.

According to the present B3LYP calculations (similarly to the experience on related Ni complexes [14, 18]), the side-on $\text{La}(\text{N}_2)_x$ structures are generally less favourable than the end-on ones. Exception is the doublet $\text{La}(\text{N}_2)_3$ being at 0 K by 23 kJ/mol lower in energy than the most stable quartet end-on $\text{La}(\text{N}_2)_3$. The thermal and entropy effects (298 K) can change somewhat (up to 13 kJ/mol) the relative energies. In terms of Gibbs free energies, also the side-on doublet $\text{La}(\text{N}_2)_2$ becomes more stable than its end-on quartet isomer. The relative stability of the side-on isomers with respect to the end-on ones decreases with the size due to the increasing steric repulsion between the ligands. The steric interactions limit the size of such structures to $x=6$. Geometry optimisations from various initial structures of $\text{La}(\text{N}_2)_7$ resulted in the escape of one N_2 from the first coordination sphere of La.

The steric interactions introduce considerable limitations also in the relative arrangement of the N_2 ligands, particularly in the larger complexes. As a result of these effects, the side-on $\text{La}(\text{N}_2)_x$ structures are in general less symmetric than the end-on ones. High symmetry was found up to $x=3$ and for $^4\text{La}(\text{N}_2)_6$ (cf. Table 4).

Both the doublet and quartet side-on $\text{La}(\text{N}_2)$ have C_{2v} symmetry due to the in-plane π orbital interaction between the La 5d π and N_2 π^* anti-bonding orbitals (Fig. 5). This is a two-electron bond in the doublet $\text{La}(\text{N}_2)$, while a one-electron bond in the quartet. The difference is characteristically demonstrated by the considerably (by 0.13 Å) shorter La–N₂ and by the somewhat longer (0.04 Å) NN bond distances of the doublet. The other donor-acceptor interaction corresponding to $\text{N}_2 \rightarrow \text{La}$ charge transfer could not be found either among the B3LYP or the CASSCF orbitals.

Though the CASPT2 and B3LYP calculations agree in the main characteristics of the electronic structure and bonding scenario in the two states, they predict opposite stability trends

Table 3 Energies (kJ/mol) of the reactions $\text{La}(\text{N}_2)_{x-1} + \text{N}_2 = \text{La}(\text{N}_2)_x$ from B3LYP calculations

$\text{La}(\text{N}_2)_x$	Spin ^a	ΔE_{ZPE}^b	ΔH_{298}	ΔG_{298}
$\text{La}(\text{N}_2)$	4	−53.7 ^c	−58.8	−31.9
$\text{La}(\text{N}_2)_2$	4	−51.4	−54.1	−17.9
$\text{La}(\text{N}_2)_3$	4	−55.3	−59.1	−30.5
$\text{La}(\text{N}_2)_4$	4	−55.0	−57.4	−25.7
$\text{La}(\text{N}_2)_5$	4	−51.6	−53.7	−19.3
$\text{La}(\text{N}_2)_6$	4	−49.5	−51.6	−12.7
$\text{La}(\text{N}_2)_7$	2	−22.9	−26.7	12.1
$\text{La}(\text{N}_2)_8$	2	−42.7	−45.6	−1.0

^a The more stable species used in the reaction energy calculation

^b From absolute energies corrected for zero-point vibrational energy

^c Calculations at the BP86/6–311+G(d)-SDD level resulted in −315.1 kJ/mol [23]

Fig. 4 Structures of side-on $\text{La}(\text{N}_2)_x$ complexes optimised by B3LYP calculations

as found for the end-on structures too (*vide supra*): at the CASPT2 level, the doublet is more stable by 8 kJ/mol, while B3LYP favours the quartet species by 2 kJ/mol (*cf.* Table 4). The CASPT2 calculations resulted in 89% contribution of the main configuration, which means a very small multiconfigurational character of doublet $\text{La}(\text{N}_2)$. Hence, the different trend may not be attributed solely to the deficiency of the B3LYP level for static correlation energy, but rather to the superimposed differences between the two theoretical levels.

It should be noted that the side-on $^2\text{La}(\text{N}_2)$ structure obtained with the mPW3PBE functional by Zhao *et al.* has an $\text{La}-\text{N}_2$ bond distance shorter by 0.1 Å with respect to the present B3LYP value and is less stable than their end-on $^4\text{La}(\text{N}_2)$ ground state by 47 kJ/mol [29]. Similar deviation in the geometry is observed by comparing the present B3LYP $^4\text{La}(\text{N}_2)$ structure with the BP86 one of Teng and Xu [23], while the relative stabilities are comparable.

In the matrix-isolation IR study by Willson and Andrews [21], IR bands in the range of 1550–1580 cm^{-1} were attributed

to end-on $\text{Ce}(\text{N}_2)$, $\text{Gd}(\text{N}_2)$ and $\text{Sm}(\text{N}_2)$ species. However, they would better fit to the side-on $\text{Ln}(\text{N}_2)$ isomers for which lower vibrational frequencies are expected (see Supplementary Information). This is the consequence of the $\eta^2\text{-Ln}-\text{N}_2$ bond, lengthening the NN triple bond with respect to the η^1 -coordinated end-on isomers (*cf.* Tables 1 and 4).

In contrast to $\text{La}(\text{N}_2)$, the orbital interactions seem to be somewhat stronger in the side-on quartet $\text{La}(\text{N}_2)_2$ than in the doublet one, as can be seen in the shorter $\text{La}-\text{N}_2$ distances (by 0.03 Å) and longer (by 0.01 Å) NN bonds with respect to those of the doublet ones. The difference can be explained by the different symmetries of the two structures. In the planar C_{2v} doublet, each La 5d π electron interacts only with one N_2 (Fig. 5) establishing two one-electron bonds. In the quartet similarly, but the two one-electron bonds are orthogonal due to the D_{2d} symmetry. The third La valence electron remains non-bonding in both species.

In spite of the above noted shorter $\text{La}-\text{N}_2$ distances, the quartet $\text{La}(\text{N}_2)_2$ is less stable than the doublet one (*cf.*

Fig. 5 Selected bonding orbitals of side-on $\text{La}(\text{N}_2)_x$ complexes

Table 4). Moreover, the B3LYP calculations underestimate the relative stability of these side-on species with respect to the end-on isomers as compared to CASPT2 theory. The latter calculations predicted relative energies of -52.9 and -18.9 kJ/mol for doublet and quartet $\text{La}(\text{N}_2)_2$, respectively, with respect to the most stable end-on form.

Comparing the side-on $\text{La}(\text{N}_2)_2$ structures with those of transition metal complexes, the D_{2d} structure of the quartet $\text{La}(\text{N}_2)_2$ agrees with that of side-on $\text{Ni}(\text{N}_2)_2$ obtained by DFT calculations by Guan et al. [18]. Apparently, the structure depends on the number and character of valence d electrons: The $5d^2$ subshell of quartet La has two unpaired electrons (ready for orbital interactions) similarly to the partly filled $3d^8$ subshell of Ni. In contrast, the $5d^1$ subshell of doublet La can provide only one electron for the bonding. Consequently, the computed structures of quartet side-on $\text{La}(\text{N}_2)_3$ and $\text{La}(\text{N}_2)_4$ agree too with those of the respective $\text{Ni}(\text{N}_2)_x$ ($x = 3-4$) complexes [18].

The optimised equilibrium structure of quartet $\text{La}(\text{N}_2)_3$ has one N_2 with perpendicular orientation to the other two N_2 -s. This is requested by the orthogonality requirement of the bonding $5d$ orbitals belonging to the three alpha spin electrons in quartet La. The requirement for full orthogonality is released in doublet $\text{La}(\text{N}_2)_3$, where the La valence $5d$ electrons

consist of two with alpha and one with beta spin. The consequence is a different structure: here, all the three N_2 ligands are arranged parallel with respect to each other. The cylinder-type C_{2v} structure is formed by one three-centred and two five-centred orbital interactions (cf. Fig. 5). This structure has a considerable stability (vide supra and Table 4).

The larger side-on $\text{La}(\text{N}_2)_x$ ($x = 4-6$) complexes, due to the less favourable asymmetric bonding scenarios and steric interactions, have ground states considerably higher in energy than the respective end-on isomers (cf. Table 4). The B3LYP and CASPT2 calculations agree in around 100 kJ/mol less stabilities of the side-on $\text{La}(\text{N}_2)_6$ species.

The larger doublet structures can be derived from the cylinder-type structure of doublet $\text{La}(\text{N}_2)_3$ by adding an N_2 to each of the terminal positions ($x = 4$ and 5 , respectively), while in $\text{La}(\text{N}_2)_6$ the cylinder is formed by four N_2 moieties (cf. Fig. 4). Similarly, the larger quartet structures can be derived from quartet $\text{La}(\text{N}_2)_3$: the characteristic feature of these structures is that they contain parallel-positioned N_2 pairs (two in $x = 4$ and 5 , while three in $x = 6$) with N-La-N angles of ca. 95° between the N_2 moieties of a pair. The N_2 pairs take orthogonal relative positions with respect to the other pairs. Such a ligand arrangement is quite unusual and reflects well the orthogonality of the three bonding $5d$ orbitals of quartet La.

Table 4 Relative energies and selected bond distances of the side-on $\text{La}(\text{N}_2)_x$ complexes from B3LYP calculations

$\text{La}(\text{N}_2)_x$	Spin	Sym	ΔE	ΔG_{298}	La-N ₂	NN
$\text{La}(\text{N}_2)^a$	2	C_{2v}	8.0	3.9	2.327	1.201
	4	C_{2v}	6.3	1.2	2.458	1.162
$\text{La}(\text{N}_2)_2^b$	2	C_{2v}	4.5	− 8.2	2.580, 2.576	1.150 (2)
	4	D_{2d}	22.3	15.7	2.548 (2)	1.160 (2)
$\text{La}(\text{N}_2)_3$	2	C_{2v}	− 22.7	− 20.4	2.560 (2), 2.546	1.152 (2), 1.156
	4	C_s	5.2	1.2	2.538 ... 2.606	1.146 ... 1.159
$\text{La}(\text{N}_2)_4$	2	C_s	19.7	23.6	2.565 ... 2.903	1.108 ... 1.146
	4	C_1	45.4	41.6	2.547 ... 2.852	1.117 ... 1.154
$\text{La}(\text{N}_2)_5$	2	C_s	61.4	63.5	2.597 ... 2.964	1.105 ... 1.142
	4	C_1	89.2	85.0	2.574 ... 2.891	1.113 ... 1.123
$\text{La}(\text{N}_2)_6^c$	2	C_1	105.5	103.7	2.587 ... 2.900	1.109 ... 1.141
	4	D_3	121.7	114.2	2.733 (6)	1.118 (6)

Relative energies with respect to the most stable end-on form are given in kJ/mol, bond distances in angstroms. In symmetric structures, the multiplicities are given in parentheses

^a The relative energies with respect to the most stable end-on form from CASPT2 calculations are − 0.7 and 7.2 kJ/mol for the doublet and quartet species, respectively

^b The relative energies with respect to the most stable end-on form from CASPT2 calculations are − 52.9 and − 18.9 kJ/mol for the doublet and quartet species, respectively

^c The relative energies with respect to the most stable end-on form from CASPT2 calculations are 90.7 and 117.3 kJ/mol for the doublet and quartet species, respectively

The computed η^2 La-N₂ bond distances agree in magnitude with the sum of single-bond covalent radii of La (1.80 Å) and N (0.71 Å) [54] and are slightly larger than the La-N₂ bonds in the respective end-on isomers (cf. Tables 1 and 4). The computed NN bond distances agree with a double-bond character in the small side-on complexes ($x=1-3$), while with a somewhat weakened triple bond in the large ones ($x=4-6$).

Table 5 Selected NBO atomic charges and populations of La valence orbitals in the side-on $\text{La}(\text{N}_2)_x$ complexes from B3LYP calculations

$\text{La}(\text{N}_2)_x$	Spin	q_{La}	q_{N}	$n(6s)$	$n(5d)$	$n(4f)$
$\text{La}(\text{N}_2)$	2	+ 0.90	− 0.45	0.85	1.12	0.10
	4	+ 0.62	− 0.31	0.90	1.41	0.06
$\text{La}(\text{N}_2)_2$	2	+ 1.04	− 0.26	0.64	1.20	0.10
	4	+ 1.22	− 0.31	0.07	1.56	0.12
$\text{La}(\text{N}_2)_3$	2	+ 1.50	− 0.24 ... − 0.26	0.13	1.18	0.14
	4	+ 1.50	− 0.22 ... − 0.31	0.13	1.15	0.17
$\text{La}(\text{N}_2)_4$	2	+ 1.29	− 0.04 ... − 0.22	0.16	1.35	0.13
	4	+ 1.31	− 0.05 ... − 0.26	0.16	1.28	0.18
$\text{La}(\text{N}_2)_5$	2	+ 1.07	− 0.02 ... − 0.17	0.18	1.53	0.12
	4	+ 1.02	− 0.02 ... − 0.22	0.19	1.52	0.16
$\text{La}(\text{N}_2)_6$	2	+ 0.76	− 0.02 ... − 0.16	0.22	1.79	0.10
	4	+ 0.75	− 0.04 ... − 0.09	0.23	1.73	0.15

Natural atomic charges and orbital populations are given in atomic units (e)

Table 5 lists the natural atomic charges in the side-on $\text{La}(\text{N}_2)_x$ complexes. Because the charge transfer interactions are more efficient with two nitrogens than with a single nitrogen in the end-on complexes, the $\text{La} \rightarrow \text{N}_2$ charge transfers to the N_2 anti-bonding orbitals are more pronounced in the side-on isomers. Consequently, these complexes are more ionic than the end-on ones. The positive charge of La is by ca. 60% larger than in the respective end-on isomers. The variation with x shows again a convex curve with the maximum at $x=3$.

The La valence orbital populations indicate considerable non-bonding 6s populations in $\text{La}(\text{N}_2)$, which is decreased in the larger complexes. Parallel, the 5d populations increase somewhat in the larger complexes, though they remain below the end-on ones mostly by ca. 0.4 e. On the other hand, the 4f orbitals are more populated (up to 0.2 e) in the side-on complexes than in the end-on ones. This implies a slight hybridisation between the La 5d and 4f orbitals in the side-on structures.

Conclusions

In the presented work, the structures and bonding properties of end-on and side-on $\text{La}(\text{N}_2)_x$ ($x=1-8$ and $1-6$, respectively) complexes were investigated by B3LYP calculations. For the $x=1, 2$ and 6 species, single-point relativistic multireference CASPT2 calculations were carried out on the optimised B3LYP geometries. These calculations confirmed the

electronic structures obtained by the B3LYP exchange–correlation functional. The dominant (mostly > 80%) electron configurations indicate a reasonable reliability of the DFT structures and bonding data. The mostly very small energy differences between the doublet and quartet isomers, however, should be treated with care.

From the two coordination modes, in general, the structures with end-on coordination were found to be more stable. The preference is particularly pronounced in the larger complexes due to the considerable steric repulsion in these side-on structures. The first coordination sphere is filled by eight and six N_2 ligands in the end-on and side-on type species, respectively. The computed bond distances correspond to weak single La– N_2 bonds, to double or considerably weakened NN triple bonds in the small complexes, while to weakened triple bonds in the larger ($x \geq 6$) ones.

The main bonding interaction is the donation of La 5d valence electrons to anti-bonding orbitals of N_2 . These directional interactions determine the equilibrium molecular structures which are in several cases less logic from steric point of view. The La $\rightarrow N_2$ charge transfers resulted in partial charges up to + 1.5 e of La and – 0.5 e of N. These generate notable electrostatic attraction between La and the N_2 ligands, which bonding interaction contributes to the stability of the complexes.

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Compliance with ethical standards

Ethical statement All ethical guidelines have been adhered.

Conflict of interest The author declares that he has no conflict of interest.

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References

- Hinrichsen S, Broda H, Gradert C, Sönksen L, Tuzek F (2012) Recent developments in synthetic nitrogen fixation. *Ann Rep Prog Chem Sect A Inorg Chem* 108:17
- Himmel H-J, Hübner O (2014) In Gade LH, Hofmann P (eds) *Molecular catalysts: structure and functional design*. Wiley-VCH, Weinheim, pp 25
- Chatt J, Pearman AJ, Richards RL (1975) The reduction of mono-coordinated molecular nitrogen to ammonia in a protic environment. *Nature* 253:39
- Yandulov DV, Schrock RR (2003) Catalytic reduction of dinitrogen to ammonia at a single molybdenum center. *Science* 301:76
- Shaver MP, Fryzuk MD (2003) Activation of molecular nitrogen: coordination, cleavage and functionalization of N_2 mediated by metal complexes. *Adv Synth Catal* 345:1061
- Fryzuk MD (2013) N_2 coordination. *Chem Commun* 49:4866
- Margulieux GW, Semproni SP, Chirik PJ (2014) Photochemically induced reductive elimination as a route to a zirconocene complex with a strongly activated N_2 ligand. *Angew Chem Int Ed* 53:9189
- Chertihin GV, Andrews L, Neurock M (1996) Reactions of laser-ablated iron atoms with nitrogen atoms and molecules. Matrix infrared spectra and density functional calculations of novel iron nitride molecules. *J Phys Chem* 100:14609
- Burdett JK, Turner JJ (1971) Binary transition metal nitrogen compounds; infrared evidence for $Ni(N_2)_x$. *J Chem Soc D Chem Commun* 885
- Huber H, Kündig EP, Moskovits M, Ozin GA (1973) Binary transition metal dinitrogen complexes. I. Matrix infrared and Raman spectra, structure and bonding of $Ni(N_2)_N$ and $Pd(N_2)_M$ ($N = 1-4$ and $M = 1-3$). *J Am Chem Soc* 95:332
- Klotzbücher W, Ozin GA (1975) Binary transition metal dinitrogen complexes. III. Metal-nitrogen stretching modes of $Ni(N_2)_n$, $Pd(N_2)_m$, and $Pt(N_2)_m$ (where $n=1-4$ and $m=1-3$). *J Am Chem Soc* 97:2672
- Manceron L, Alikhani ME, Joly HA (1998) Infrared matrix isolation and DFT study of NiN_2 . *Chem Phys* 228:73
- Himmel H-J, Manceron L (2005) $Ni(N_2)_4$ revisited: an analysis of the $Ni-N_2$ bonding properties of this benchmark system on the basis of UV/Vis, IR and Raman spectroscopy. *Dalton Trans* 2615
- Hübner O, Manceron L, Himmel H-J (2014) On the electronic structure and photochemistry of coordinatively unsaturated complexes: the case of nickel bis-dinitrogen, $Ni(N_2)_2$. *Chem Eur J* 20: 17025
- Wang C-J, Xu X (2006) Density functional theory study of the interactions between an iron atom and a dinitrogen molecule I. The end-on linear and bent structures. *J Theor Comput Chem* 5:489
- Bauschlicher Jr CW, Langhoff SR, Barnes LA (1989) Bonding in zerovalent Ni compounds: NiN_2 and $Ni(N_2)_4$ compared with $NiCO$ and $Ni(CO)_4$. *Chem Phys* 129:431
- Ciullo G, Rosi M, Sgamellotti A, Floriani C (1991) On the relative stability of side-on and end-on coordination of dinitrogen to nickel (O): “ab initio” calculations on the model compounds $[NiN_2]$ and $[Ni(Ph_3)_2 N_2]$. *Chem Phys Lett* 185:522
- Guan J, Li Q (2005) Structures and kinetic stabilities of the possible complexes of mononuclear Ni and $(N_2)_x$ ($x = 1-4$). *J Phys Chem A* 109:9875
- Zhao R-N, Lu Z-C (2016) A density functional calculation on W doped N_n ($n=1-9$) clusters. *Main Group Chem* 15:243
- Chertihin GV, Bare WD, Andrews L (1998) Reactions of yttrium and lanthanum atoms with nitrogen. Infrared spectra of the metal nitrides and dinitrogen complexes in solid argon and nitrogen. *J Phys Chem A* 102:3697
- Willson SP, Andrews L (1998) Characterization of the reaction products of laser-ablated early lanthanide metal atoms with dinitrogen. Infrared spectra of LnN , LnN_2 , $(LnN)_2$, and $Ln(NN)_x$ molecules. *J Phys Chem A* 102:10238
- Willson SP, Andrews L (1999) Characterization of the reaction products of laser-ablated late lanthanide metal atoms with dinitrogen. Matrix IR spectra of LnN , $(LnN)_2$, and $Ln(NN)_x$ molecules. *J Phys Chem A* 103:1311
- Teng Y-L, Xu Q (2008) Matrix isolation infrared spectroscopic studies and density functional theory calculations of the MNN , $(MN)_2$ ($M = Y$ and La), and Y_3NN molecules. *J Phys Chem A* 112:3607
- Campazzi E, Solari E, Floriani C, Scopelliti R (1998) The fixation and reduction of dinitrogen using lanthanides: praseodymium and neodymium meso-octaethylporphyrinogen–dinitrogen complexes. *Chem Commun* 2603

25. Evans WJ, Allen NT, Ziller JW (2002) Expanding divalent organolanthanide chemistry: the first organothulium (II) complex and the in situ organodysprosium (II) reduction of dinitrogen. *Angew Chem Int Ed* 41:359
26. Gardiner MG, Stringer DN (2010) Dinitrogen and related chemistry of the lanthanides: a review of the reductive capture of dinitrogen, as well as mono- and di-aza containing ligand chemistry of relevance to known and postulated metal mediated dinitrogen derivatives. *Materials* 3:841
27. Evans WJ, Lee DS (2011) Early developments in lanthanide-based dinitrogen reduction chemistry. *Can J Chem* 83:375
28. Studt F, Tuzek F (2006) Theoretical, spectroscopic, and mechanistic studies on transition-metal dinitrogen complexes: implications to reactivity and relevance to the nitrogenase problem. *J Comput Chem* 27:1278
29. Zhao R-N, Chen R, Sun S, Zhang Y-J, Yuan Y-H (2017) Geometries, electronic and magnetic properties of dinitrogen adsorbed on lanthanide element LnN_2 ($\text{Ln} = \text{La-Lu}$) systems: a density functional investigation. *J Mol Struct* 1141:600
30. Ermilov AY, Nemukhin AV, Kovba VM (1999) Characterization of structures and spectra of holmium complexes formed in the CO and N_2 matrices. *Mendeleev Commun* 9:88
31. Cundari TR, Stevens WJ (1993) Effective core potential methods for the lanthanides. *J Chem Phys* 98:5555
32. Martin WC, Zalubas R, Hagan L (1978) Atomic energy levels—the rare-earth elements. The spectra of lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. National Bureau of Standards, U.S. Department of Commerce, Washington, US
33. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery Jr 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 C, 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 D.01. Gaussian, Inc., Wallingford CT
34. Becke AD (1993) Density-functional thermochemistry. III. The role of exact exchange. *J Chem Phys* 98:5648
35. 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* 37:785
36. Dolg M, Stoll H, Preuss H (1989) Energy-adjusted ab initio pseudopotentials for the rare earth elements. *J Chem Phys* 90:1730
37. Cao X, Dolg M (2002) Segmented contraction scheme for small-core lanthanide pseudopotential basis sets. *J Mol Struct (THEOCHEM)* 581:139
38. Dunning Jr TH (1989) Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J Chem Phys* 90:1007
39. Grimme S, Antony J, Ehrlich S, Krieg H (2010) A consistent and accurate ab initio parameterization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J Chem Phys* 132:154104
40. Reed AE, Curtiss LA, Weinhold F (1988) Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint. *Chem Rev* 88:899
41. Glendening ED, Badenhoop JK, Reed AE, Carpenter JE, Bohmann JA, Morales CM, Landis CR, Weinhold F (2013) NBO 6.0. Theoretical chemistry institute, University of Wisconsin, Madison, US
42. Glendening ED, Landis CR, Weinhold F (2013) NBO 6.0: natural bond orbital analysis program. *J Comput Chem* 34:1429
43. Roos BO (1987) In: Lawley KP (ed) *Advances in chemical physics, Ab Initio Methods in Quantum Chemistry - II*. Wiley, Chichester, pp 399
44. Andersson K, Malmqvist P-Å, Roos BO, Sadlej A, Wolinski K (1990) Second-order perturbation theory with a CASSCF reference function. *J Phys Chem* 94:5483
45. Andersson K, Malmqvist P-Å, Roos BO (1992) Second-order perturbation theory with a complete active space self-consistent field reference function. *J Chem Phys* 96:1218
46. Douglas N, Kroll NM (1974) Quantum electrodynamical corrections to the fine structure of helium. *Ann Phys* 82:89
47. Hess BA (1986) Relativistic electronic-structure calculations employing a two-component no-pair formalism with external-field projection operators. *Phys Rev A* 33:3742
48. Roos BO, Lindh R, Malmqvist P-Å, Veryazov V, Widmark P-O (2008) New relativistic atomic natural orbital basis sets for lanthanide atoms with applications to the Ce diatom and LuF_3 . *J Phys Chem A* 112:11431
49. Roos BO, Lindh R, Malmqvist P-Å, Veryazov V, Widmark P-O (2004) Main group atoms and dimers studied with a new relativistic ANO basis set. *J Phys Chem A* 108:2851
50. Krisiloff DB, Krauter CM, Ricci FJ, Carter EA (2015) Density fitting and Cholesky decomposition of the two-electron integrals in local multireference configuration interaction theory. *J Chem Theory Comput* 11:5242
51. Veryazov V, Malmqvist P-Å, Roos BO (2011) How to select active space for multiconfigurational quantum chemistry? *Int J Quantum Chem* 111:3329
52. Karlström G, Lindh R, Malmqvist P-Å, Roos BO, Ryde U, Veryazov V, Widmark P-O, Cossi M, Schimmelpennig B, Neogrady P, Seijo L (2003) MOLCAS: a program package for computational chemistry. *Comput Mater Sci* 28:222
53. Aquilante F, Autschbach J, Carlson RK, Chibotaru LF, Delcey MG, De Vico L, Galván IF, Ferré N, Frutos LM, Gagliardi L, Garavelli M, Giussani A, Hoyer CE, Li Manni G, Lischka H, Ma D, Malmqvist P-Å, Müller T, Nenov A, Olivucci M, Pedersen TB, Peng D, Plasser F, Pritchard B, Reiher M, Rivalta I, Schapiro I, Segarra-Martí J, Stenrup M, Truhlar DG, Ungur L, Valentini A, Vancioille S, Veryazov V, Vysotskiy VP, Weingart O, Zapata F, Lindh R (2016) MOLCAS 8: new capabilities for multiconfigurational quantum chemical calculations across the periodic table. *J Comput Chem* 37:506
54. Pykkö P, Atsumi M (2009) Molecular single-bond covalent radii for elements 1–118. *Chem Eur J* 15:186
55. Pykkö P, Atsumi M (2009) Molecular double-bond covalent radii for elements Li-E112. *Chem Eur J* 15:12770