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Dinitrogen Activation by the Ti_2N_2 Molecule: A Matrix Isolation Study

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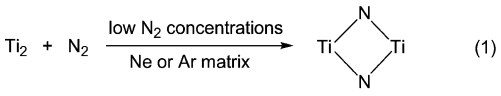
Herein we report on matrix isolation experiments carried out for the reaction of $Ti_2(\mu\text{-}N)_2$ with N_2 in Ne and pure N_2 matrices. N_2 complexes with various degrees of N_2 activation are formed in the course of this reaction.

Introduction

One of the main research themes of our groups is the evaluation of the differences in reactivity between single metal atoms and small metal atom clusters. In the case of Ti it was shown that single atoms in their electronic ground state do not react with N_2, presumably because of significant σ repulsion. Ti atoms exhibit a $3d^24s^2$ (^3F) electronic ground state and a $3d^34s^1$ (^5F) excited (metastable) state at 77.2 kJ mol^{-1} higher energy. It has been shown in other cases that the depopulation of the valence s orbital increases the reactivity. Hence in the case of the Co-N_2 complex the $3d^84s^1$ configuration is more reactive than the $3d^74s^2$ configuration as there is less σ repulsion and more possibility for π back donation.[1,2] After photolytical activation Ti atoms indeed form a weakly bound N_2 complex.[3] But from the work of Honma et al.[4] a single Ti atom in its electronic ground state does not react with N_2. Solid Ti metal, on the other hand, only reacts at very high temperatures, although the reaction to give the nitride TiN is of course highly exothermic. In previous experiments we addressed the question if the reactivity increases for metal dimers or small metal clusters. Prior to this study, a thorough analysis of the Ti_2 dimer in a combined experimental and quantum chemical approach was necessary.[5,6] Using Resonance Raman spectroscopy, a series of overtones of the Ti–Ti stretching fundamental of the dimer was traced which was used to estimate the dissociation energy of Ti_2 to be ca. 115 kJ mol^{-1}.[5,7] Quantum chemical MRCI calculations argued for a somewhat higher value (ca. 150 kJ mol^{-1}).[6] The calculations also predicted the electronic ground state to be $^3\Delta_g$. Absorption spectroscopy was then employed to obtain information about electronically excited states. The experiments thus showed that the Ti_2 dimer is a relatively weakly bound species. In the light of these facts it came as surprise that experiments by us clearly showed that Ti_2 reacts with N_2 in Ar or Ne matrices.[8] At low concentrations of N_2 in an Ar or Ne matrix, the N≡N triple bond is completely cleaved, and a four-membered, rhombic $Ti_2(\mu\text{-}N)_2$ ring formed [see Equation (1)].[9] High level quantum chemical (MRCISD+Q) calculations predicted an ^1A_g electronic ground state for this species, in disagreement to earlier DFT (BP86/Watchers + spd) results suggesting a $^3B_{1u}$ electronic ground state.[2] It proved also possible to analyse parts of the electronic excitation spectra for this nitride, which can be regarded as the smallest fraction of solid TiN. The molecule features one unpaired electron at each Ti atom, pointing to an increased nucleophilic character. Therefore $Ti_2(\mu\text{-}N)_2$ should be highly reactive towards electrophiles and also ready to activate multiple bonded molecules such as N_2. Herein we report on the reaction of $Ti_2(\mu\text{-}N)_2$ with N_2 and will show that N_2 complexes with different degrees of NN bond activation emerge. The results of our studies might be of relevance for catalytic dinitrogen activation and reduction at TiN nanoparticles.[10]



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Results and Discussion

Figure 1 displays the IR spectra recorded for a Ne matrix containing Ti and N_2 in different molar ratios N_2/Ne. The spectrum at low N_2 concentrations (N_2/Ne = 0.5:1000) was dominated by the bands at 782.3 and 774.8 cm^{-1} due to $Ti_2(\mu\text{-}^{14}N)_2$ [8] showing the Ti isotopic pattern characteristic of the presence of two equivalent Ti atoms. At the low en-

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ergy side of these bands, several weak features appeared (maxima at 768, 763, 760 and 756 cm^{-1}). A weak band was also observed at 850 cm^{-1}. At the same time, the NN stretching region contained three bands. One at 2182.5 cm^{-1} and two further ones at 2158.0 and 2094.5/2089.9 cm^{-1}, which can be assigned to two relatively weakly coordinated N_2 complexes of $Ti_2(\mu\text{-}^{14}N)_2$. The experiments were repeated with $^{15}N_2$. The bands at 2182.5 cm^{-1} shifted to 2111.4 cm^{-1}, while those at 2158.0 and 2094.5/2089.9 cm^{-1} now occurred at 2086.5 and 2021.0 cm^{-1}. On the low-energy side of the $Ti_2(\mu\text{-}^{15}N)_2$ absorptions, bands at 748, 744, 740 and 737 cm^{-1} appeared. Finally in experiments with equimolar mixtures of $^{14}N_2$ and $^{15}N_2$, new bands at 2137 and 2041 cm^{-1} were visible in addition to the bands observed in the experiments using $^{14}N_2$ and $^{15}N_2$ separately. The bands can be assigned to end-on coordinated N_2 complexes of the general formula $[(N_2)_nTi(\mu\text{-}N)_2Ti(N_2)_m]$. The band at 2182.5 cm^{-1} in the NN stretching region belongs to $[Ti(\mu\text{-}N)_2Ti(N_2)]$ and the two bands at 2158.0 and 2094.5/2089.9 belong to either $[\{(N_2)Ti\}_2(\mu\text{-}N)_2]$ or $[Ti(\mu\text{-}N)_2Ti(N_2)_2]$. Thus at relatively small N_2 concentrations, $Ti_2(\mu\text{-}N)_2$ reacts with N_2 to give relatively weakly coordinated N_2 complexes without electron transfer occurring from a metal centered orbital into one of the π^* orbitals of N_2. In addition, weaker features were visible at 1840.6 and 1710.0 cm^{-1}. In experiments relying on $^{15}N_2$ in place for $^{14}N_2$, these two bands shifted to 1779.5 and 1654.1 cm^{-1}. Their position and the large isotopic shift indicate that they belong to NN stretches of more activated N_2 units. The bands grew significantly with increasing concentration of N_2 in the matrix, while the bands due to $Ti_2(\mu\text{-}N)_2$ decreased. Additional information was obtained from the experiments with $^{14}N_2/^{15}N_2$ mixtures. Thus no extra band appeared in these experiments, and the spectrum turned out to be identical with the superposition of those obtained with $^{14}N_2$ and $^{15}N_2$ separately in the regions around these two bands. Finally, experiments with mixtures containing $^{14}N^{15}N$ resulted in two new bands at 1810 and 1682 cm^{-1}, showing that both N atoms are equivalent in the strongly coordinated sub-unit. Possible species responsible for these two absorptions are products in which $Ti_2(\mu\text{-}N)_2$ is bound to (in addition to terminally bound N_2 showing at 2067, 2033 and 2011 cm^{-1}) one N_2 side-on coordinated to one of the two metals or to a N_2 unit bridging both metals in a $\mu\text{-}\eta^1\text{:}\eta^1$ fashion.

Finally, experiments were conducted in solid N_2 matrices. Figure 2 displays parts of the resulting IR spectrum for $^{14}N_2$, $^{15}N_2$ and $^{14}N_2/^{15}N_2$ matrices. The two bands at 1840.6 and 1710.0 cm^{-1} disappeared. Instead, a broad and intense band at 1407 cm^{-1} (main matrix site) appeared which shifted to 1363 cm^{-1} in experiments with $^{15}N_2$ in place for $^{14}N_2$. The $^{14}N_2/^{15}N_2$ experiments (no extra maxima) confirmed that the band arises from just one N_2 unit which is considerably activated. On the basis of a comparison with the NN stretches of other molecules (e.g. 1529 cm^{-1} in *trans* diazene, HNNH[11]) it can be concluded that in the product complex both electrons at the Ti atoms were transferred to one N_2 unit, leading to a doubly bonded N_2 group which can be compared with the N_2^{2-} dianion. From the presence of one such unit and the IR intensities it can be concluded that the product is non-centrosymmetric. The presence of bands around 700 cm^{-1} (see Figure 2) signals the conservation of the $Ti_2(\mu\text{-}N)_2$ ring (which, however, most likely deviates from planarity). The absence of any additional bands in the experiments with $^{14}N_2/^{15}N_2$ is also in agreement to the presence of this ring which is formed in a concerted dimolecular reaction between Ti_2 and N_2 and argues for a negligible electron coupling between the N_2^{2-} unit and the $Ti_2(\mu\text{-}N)_2$ ring. The NN stretching region displayed four large bands at 2263, 2255, 2133 and 2098 cm^{-1} which were observed to shift to 2188, 2179, 2061 and 2028 cm^{-1} upon replacing $^{14}N_2$ by $^{15}N_2$ and can all be assigned to the same product of the reaction of $Ti_2(\mu\text{-}N)_2$ with N_2. The pattern visible in the experiments conducted with $^{14}N_2/^{15}N_2$ (four additional bands at 2261, 2185, 2118 and 2043 cm^{-1}) is in line with the presence of four N_2 units attached to each of the chemically-equivalent Ti atoms. A number of additional bands [most of them belonging to deformation modes, e.g. δ(NNTi) or δ(NTiN)] can be assigned to the same species

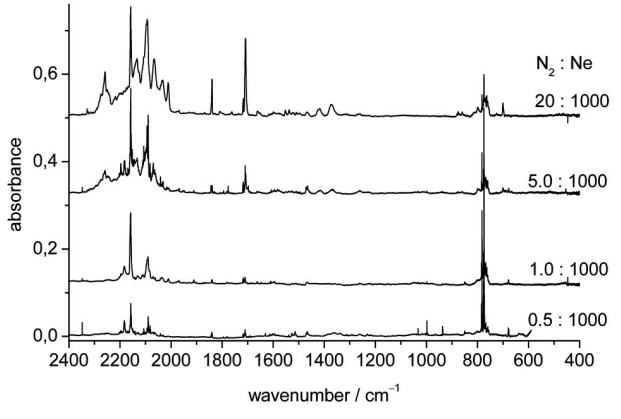

Figure 1. IR spectra recorded for reaction of $Ti_2(\mu\text{-}N)_2$ with N_2 in a Ne matrix at different concentrations of N_2.

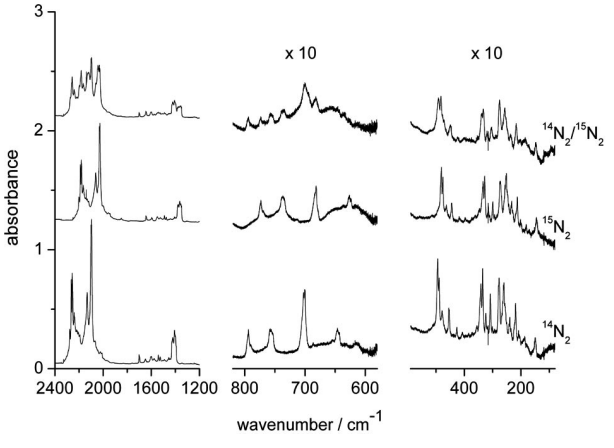

Figure 2. IR spectra recorded for the reaction of Ti_2 with excess N_2 in a pure N_2 matrix (Ti/N_2 = 3.15:1000).

on the basis of experiments with different Ti concentrations as well as annealing and photolysis experiments (see Figure 3 as well as Figures S2 and S3 in the Supporting Information) and are all provided in Table 1. In total as many as 27 bands of this complex were detected.[12]

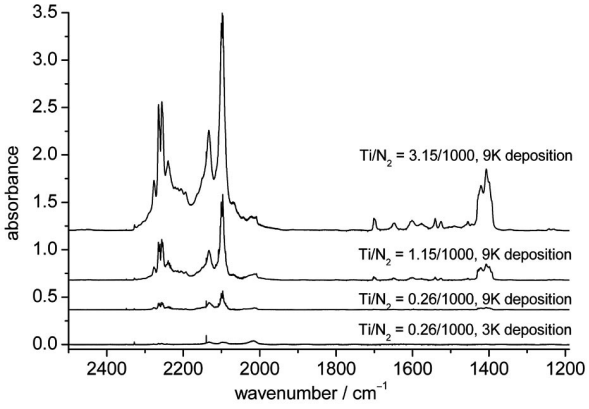

Figure 3. IR spectra recorded for the reaction between titanium and dinitrogen in N_2 matrices for different Ti/N_2 molar ratios. The two spectra for Ti/N_2 = 0.26:1000 show that product formation requires mild annealing of the matrix.

Table 1. Comparison between the observed wavenumbers [cm^{-1}] for the product formed in neat N_2 matrices, [{$(N_2)_4Ti$}$_2$(μ-N)$_2$(μ-η^2:η^2-N_2)].

$^{14}N_2$	$^{15}N_2$	$^{14}N_2/^{15}N_2$ additional maxima
2263	2188	2261
2254	2179	2185
2133	2061	2118
2098	2028	2043
1407[c]	1363[c]	[a]
858	835	[a]
793	773	[a]
757	736	[a]
701	682	[a]
645	625	[a]
494	481	491
489	476	483
479	464	[b]
455	445	450
426	419	423
408	397	402
342	334	339
336	329	333
326	316	320
308	300	305
278	274	276
261	253	257
240	233	237
219	213	216
209	202	[a]
187	182	185
150	146	147

[a] No additional bands. [b] Too weak and broad to be detected. [c] Only the main matrix-site values are quoted.

Titanium concentration effects (see Figure 3) clearly show that i) in conditions where isolation of Ti atoms is predominant (3 K deposition and low Ti content) these products are but barely detectable and ii) the growth of these product absorption bands with increasing titanium content is not linear and is therefore consistent with a $Ti_2(N_2)_n$ stoichiometry. Figure 4 shows on the left side an illustration of the molecular structure consistent with the spectroscopic data for this product, which can be formulated as [{$(N_2)_4Ti$}$_2$(μ-N)$_2$(μ-η^2:η^2-N_2)].[13] The right side shows the anionic dinuclear Ti complex [{[$(Me_3Si)_2N$]$_2$-Ti}$_2$(μ-η^2:η^2-N_2)$_2$]$^-$ featuring two highly activated N_2 units.[14] This latter complex was synthesized {with [Li(TMEDA)$_2$]$^+$ as counterion} as one of the products of the reaction between *trans*-[(TMEDA)$_2$TiCl$_2$] and LiN(SiMe$_3$)$_2$ in an N_2 atmosphere. The NN stretches were reported to occur at 1380 and 1360 cm^{-1}, in close proximity to the wavenumber of the band observed for [{$(N_2)_4Ti$}$_2$(μ-N)$_2$(μ-η^2:η^2-N_2)] (1407 cm^{-1}). The formal oxidation states of the Ti atoms in [{[$(Me_3Si)_2N$]$_2$Ti}$_2$(μ-η^2:η^2-N_2)$_2$]$^-$ are +I and +II. However, if the N_2 units are described as N_2^{2-}, they would change to +III and +IV. In [{$(N_2)_4Ti$}$_2$(μ-N)$_2$(μ-η^2:η^2-N_2)], the formal oxidation state is +III for both Ti atoms, and increases to +IV if the bridging N_2 unit is considered as an N_2^{2-} dianion.

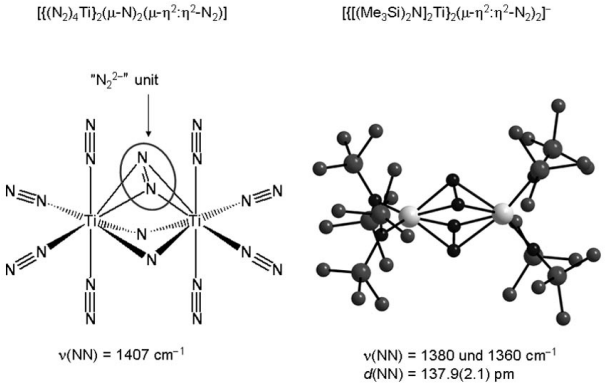

Figure 4. Visualization of the likely structure of the [{$(N_2)_4Ti$}$_2$(μ-N)$_2$(μ-η^2:η^2-N_2)] complex formed by reaction of $Ti_2(\mu$-N)$_2$ and an excess of N_2 in an N_2 matrix and of the anionic [{[$(Me_3Si)_2N$]$_2$-Ti}$_2$(μ-η^2:η^2-N_2)$_2$]$^-$ complex as derived from X-ray diffraction (see ref. 10).

Annealing experiments (up to 30 K) gave no evidence for the formation of additional products or for the decomposition of [{$(N_2)_4Ti$}$_2$(μ-N)$_2$(μ-η^2:η^2-N_2)] (see Figure S1 in the Supporting Information). However, photolysis ($\lambda \approx 500$ nm) brought about a slow decay of the bands due to this complex and the appearance of new bands (see Figures S1 and S2 in the Supporting Information). Thus [{$(N_2)_4Ti$}$_2$(μ-N)$_2$-(μ-η^2:η^2-N_2)] can be photo-converted into another dinitrogen complex, presumably still featuring a $Ti_2(\mu$-N)$_2$ ring. Finally, we recorded a series of Raman spectra in solid N_2 matrices. While no signal due to a titanium-dinitrogen complex could be traced in Raman spectra of Ne matrices containing small amounts of N_2 (due to lack of sufficient Raman intensity), spectra recorded in solid N_2 (and excited by laser light at λ = 488 nm) showed extremely intense resonance Raman signals which could all be assigned to a single species (see Figures S3–S6 in the Supporting Information). The spectra have some similarities to the IR spectra, e.g. a strong signal in the region around 1400 cm^{-1}, also with

spectral characteristics of a symmetrically bonded N_2^{2-} subunit. However, the signals clearly do not belong to [{$(N_2)_4$-Ti}$_2$(μ-N)$_2$(μ-η^2:η^2-N_2)], but presumably to the complex formed from this species by the action of the Raman laser light, differing in the number or arrangement of the end-on coordinated groups.

Conclusions

In summary we have shown that the observed products of the matrix reaction between $Ti_2(\mu\text{-}N)_2$ and N_2 heavily depend on the N_2 concentration. On variation of this concentration, molecules are formed in which N_2 is either weakly complexed (at low concentrations) or highly activated (in neat N_2 matrixes) through interaction of an N_2 ligand with a symmetrically bridging structure on the $Ti_2(\mu\text{-}N)_2$ ring. A detailed analysis of the reaction products by quantum chemical calculations should represent a challenge for theoretical chemists.

Experimental Section

General: N_2 complexes of $Ti_2(\mu\text{-}N)_2$ were formed by co-condensing Ti vapor and dilute N_2/Ne mixtures, using the 2.8 K set-up described previously.[8,15] A Ti/Mo filament (Goodfellow, 85% Ti and 15% Mo), was heated at 1400–1600 °C to generate the Ti metal vapor. The metal deposition rate was monitored with the aid of a quartz microbalance and varied from 1.5 to 20 nanomol min^{-1}. For most samples, this corresponded to 50–500 ppm Ti/Ne or Ti/N_2 molar ratios. High purity Ne (Air Liquide, France 99.9995%), N_2 (Air Liquide, France; 99.998%) and $^{15}N_2$ (Isotec, USA, 99.0% ^{15}N) were used to prepare the N_2/Ne mixtures. Scrambled nitrogen ($^{14}N_2$, $^{14}N^{15}N$, $^{15}N_2$), was prepared by mixing equal quantities of N_2 and $^{15}N_2$ in a high voltage, 100 mA DC discharge. The spectroscopic set-up and procedures are identical to those described previously.[15] The absorption spectra were taken here over the 20000–80 cm^{-1} range *on the same samples* with a resolution varied from 0.02 cm^{-1} to 0.1 cm^{-1}. Bare mirror backgrounds, recorded prior to sample deposition, were used as references in processing the sample spectra. The spectra were subsequently subjected to baseline correction to compensate for infrared light scattering and interference patterns.

Supporting Information (see also the footnote on the first page of this article): Additional IR spectra recorded in solid dinitrogen matrices and Raman spectra recorded in solid dinitrogen matrices.

Acknowledgments

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