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# Polyisocyanides of Titanium

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Neutral Ti[CN]$_n$ complexes have been investigated with quantum chemistry techniques. According to our theoretical predictions, these complexes are shown to prefer isocyanide arrangements. Therefore, these compounds are good candidates to be the first polyisocyanides to be characterized. The theoretical calculations predict Ti(NC)$_4$, a methane-like tetrahedral structure with four isocyanide ligands, as the most stable neutral complex. The fact that the isocyanide ligand is a better $\pi$-donor than the cyanide one seems to be the key factor for the preference for isocyanides in neutral titanium complexes.

## Introduction

The ability of the cyanide ion to form complexes with transition metals is very well-known, ferrocyanide being a prototypical example. In all known complexes the cyanide ion is bonded to the metal through the carbon atom, thus corresponding to the cyanide form. However, the monocyanides of transition metals do not always behave in the same way. Very recently a number of experiments have been devoted to elucidate the structure of transition metal monocyanides. We will only refer to the experimental work on first-row transition metals. Ziurys and co-workers[1−5] have observed, through rotational spectroscopy, the following cyanides: CuCN, ZnCN, NiCN, CoCN, and CrCN. Nickel cyanide has also been studied by Kingston et al.,[6] whereas Boldyrev et al.[7] have studied the photoelectron spectrum of CuCN$^-$. On the other hand, laser fluorescence excitation experiments by Lie and Dagdigian[8] led to the observation of iron isocyanide, FeNC.

Different theoretical studies have been carried out on individual systems. Boldyrev et al.[7] studied the CuCN$^-$ anion and its neutral counterpart. NiCN has been the subject of a preliminary theoretical study by Bauschlicher,[9] whereas Paul et al.[10] studied both the cyanide and isocyanide forms. DeYonker et al.[11] and Hirano et al.[12] studied the FeCN/FeNC system, whereas Nelin et al.[13] and Dietz et al.[14] carried out studies on CuCN and CuNC. In a recent paper[15] we have carried out a systematic study of first-row transition metal cyanides and isocyanides. The theoretical predictions are in agreement with the experimental observations. In general, late transition metals (Co−Zn) and Cr prefer the cyanide arrangement. On the other hand, early transition metals (Sc, Ti, V), as well as Mn and Fe, favor the isocyanide isomer. Nevertheless, for the V[CN], Mn[CN], and Fe[CN] systems both isomers lie very close in energy.

In view of these results a question emerges: is it possible to obtain polyisocyanides? In the present work we deal with this question. We have selected titanium, an element forming interesting new materials bonded to carbon. As we have pointed out, the isocyanide form is preferred over the cyanide form in the monomer Ti[CN]. Therefore, the main purpose of the present work is to predict the molecular structure and stability of Ti[CN]$_n$ compounds.

## Computational Methods

Quantum chemical calculations have been carried out in order to predict the structures of Ti(CN)$_n$ compounds. The geometries and vibrational frequencies have been computed employing density functional theory (DFT). In particular we have employed the B3LYP functional, which comprises the Lee−Yang−Parr[16] correlation functional in conjunction with a hybrid exchange functional proposed by Becke.[17] We have employed in our calculations the 6-311+G(d) basis set. This basis set is constructed employing the split-valence 6-311G for carbon and nitrogen atoms,[18] supplemented with a set of polarization d functions. For titanium this basis set employs the Wachters[19] and Hay[20] basis set with the scaling factor of Ragavachari and Trucks,[21] corresponding to a contraction scheme of [10s/7p/4d/1f]. In addition, in order to check the effect of including more polarization functions, we have carried out calculations with the 6-311+G(2df) basis set, which means [10s/7p/4d/2f/1 g] for titanium.

Electronic energies have been refined by means of single-point calculations at the CCSD(T) level[22] (coupled cluster single- and double-excitation model augmented with a noniterative treatment of triple excitations). All calculations were carried out with the Gaussian-98 program package.[23]

## Results and Discussion

We have searched for homoleptic and heteroleptic compounds formed by titanium with CN/NC. Therefore, the general formula can be written as Ti(CN)$_x$(NC)$_y$. Taking $n = x + y$, we have considered in the present work compounds corresponding to $n = 1−6$. In Figure 1 we show the geometrical parameters for the homoleptic compounds, the first value corresponding to the cyanide form, whereas the second value is for the isocyanide form. It must be pointed out that for $n = 5$ and $n = 6$ compounds only the isocyanide form was characterized as a true minimum. The cyanide forms exhibit imaginary frequencies. The attempts to obtain low-symmetry true minima for the cyanides were unsuccessful. Only heteroleptic compounds, with mixed cyanide and isocyanide ligands, were characterized as true minima.

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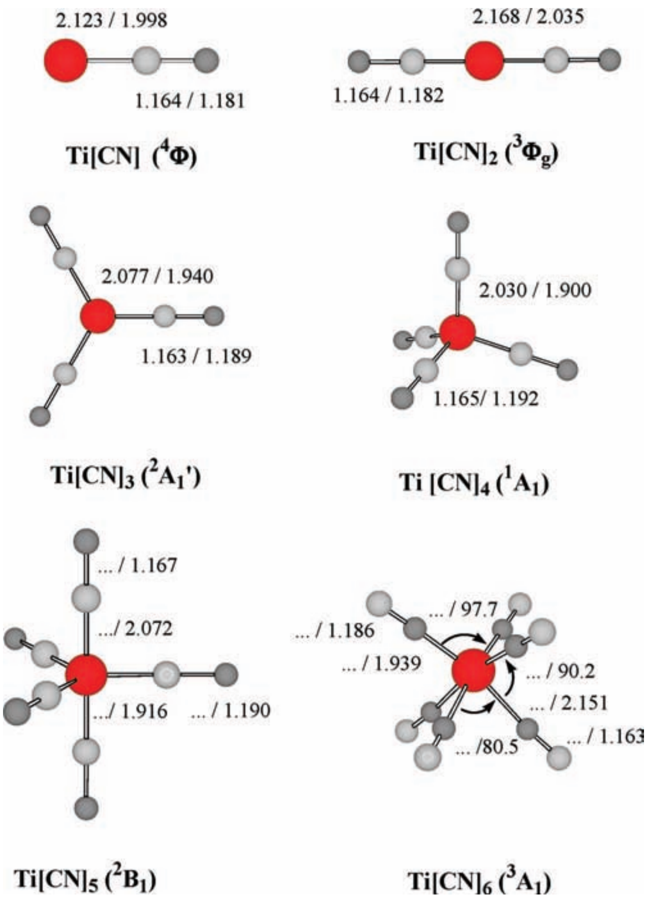

**Figure 1.** Geometrical parameters for the homoleptic Ti[CN]$_n$ complexes. Bond distances are given in angstroms, and bond angles are in degrees: first value, cyanide isomer; second value, isocyanide isomer.

However, all of them were found to lie higher in energy than the isocyanide isomer.

Bond distances exhibit expected patterns. C−N distances for cyanides are very close to the bond length observed for the CN radical at the same level of theory (namely, 1.166 Å), whereas for isocyanides the C−N distance is usually noticeably longer (within the range of 1.181−1.192 Å). As expected Ti−C distances are longer than Ti−N bond lengths. All Ti[CN]$_n$ species have typical structures except Ti(NC)$_6$. Cyanides and isocyanides of Ti[CN] and Ti[CN]$_2$ are linear, whereas Ti[CN]$_3$ has a planar structure. Ti[CN]$_4$ presents a tetrahedral geometry, and Ti[CN]$_5$ has a trigonal bipyramidal structure. On the other hand, the octahedral structure for Ti(NC)$_6$ has imaginary frequencies, and only a structure corresponding to $C_{3v}$ symmetry could be characterized as a true minimum.

The computed energy differences between the homoleptic cyanide and isocyanide Ti[CN]$_n$ isomers are shown in Table 1. We only provide values up to $n = 4$, since for $n = 5$ and 6 the cyanide forms cannot be obtained. Both levels of theory, B3LYP and CCSD(T), agree basically in their predictions. It is readily seen that in all cases the isocyanide isomer is preferred, and this preference increases with the number of ligands. Furthermore, including additional polarization functions has only a very minor effect, supporting the preference for the isocyanide isomers. In order to analyze more deeply this behavior we have computed the energy differences between the different heteroleptic complexes and the all-cyanide form. The results are depicted in Figure 2. It seems that the preference for the isocyanide ligand is favored by the presence of other cyanide ligands. This trend is reflected in the higher stabilization obtained by the exchange of a cyanide ligand by an isocyanide observed in the series Ti[CN]$_2$, Ti[CN]$_3$, and Ti[CN]$_4$. On the other hand, within a series with the same total number of ligands, as the number of isocyanide ligands increases, the stabilization energy obtained by the exchange cyanide−isocyanide is lowered.

**TABLE 1: Energy Differences (kcal/mol), Including ZPVE Corrections, between the Homoleptic Isocyanide and Cyanide Ti[CN]$_n$ Complexes**[a]

| | B3LYP/ 6-311+G(d) | CCSD(T)/ 6-311+G(d) | CCSD(T)/ 6-311+(2df) |
|---|---|---|---|
| Ti[CN] | −2.63 | −3.04 | −2.56 |
| Ti[CN]$_2$ | −7.41 | −3.79 | −3.99 |
| Ti[CN]$_3$ | −19.96 | −16.70 | −16.92 |
| Ti[CN]$_4$ | −27.01 | −24.42 | −24.77 |

[a] A negative value indicates that the isocyanide isomer is more stable than the cyanide one.

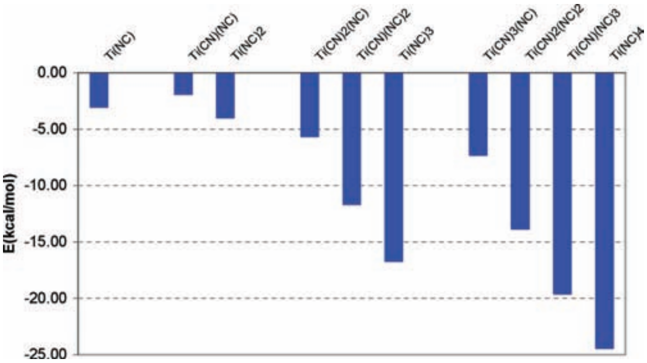

**Figure 2.** Energy differences (kcal/mol) associated to the exchange cyanide−isocyanide in heteroleptic Ti(CN)$_x$(NC)$_y$ complexes.

We have carried out a natural bond orbital (NBO) analysis[24] in order to shed light into the preference for the isocyanide titanium complexes. In particular, the second-order perturbative estimates of “donor−acceptor” (bond−antibond) interactions[24] reveal very interesting features. For example, in the case of Ti[CN]$_4$ complexes the sum of the “$\sigma$” interactions are roughly of the same magnitude for both cyanide and isocyanide isomers. These $\sigma$ interactions include n(C) → $\sigma$*(Ti−N), n(C) → n*(N), $\sigma$(Ti−N) → n*(C), and 3s(Ti) → $\sigma$*(N−C) for the isocyanide isomers, and the corresponding terms, n(N) → $\sigma$*(Ti−C), n(N) → n*(C), $\sigma$(Ti−C) → n*(N), and 3s(Ti) → $\sigma$*(C−N), for the cyanide isomer. On the other hand, the main difference is observed in the “$\pi$” interactions. The total amount of $\pi$ back-donation, $\pi$(N−C) → d(Ti), in Ti(NC)$_4$ is 106.5 kcal/mol (roughly 27 kcal/mol per bond), whereas in the case of (TiCN)$_4$, the $\pi$(C−N) → d(Ti) interaction corresponds to 42.4 kcal/mol (about 11 kcal/mol per bond). Therefore, the NBO analysis suggests that to a large extent the preference for the isocyanide conformation in titanium complexes is essentially due to the fact that isocyanide is a better $\pi$-donor than cyanide is. This ability of $\pi$-donation is important in the case of titanium with vacant d orbitals.

Having established that the isocyanide complexes are preferred over the cyanide ones, the crucial question that remains is the relative stability of Ti(NC)$_n$ complexes. In Table 2 we provide the energy values associated to the process of complexation by a NC ligand in Ti(NC)$_n$ compounds (in the case of the formation of TiNC this value is already reported in ref 15, namely, 108.47 and 98.76 kcal/mol at the B3LYP and CCSD(T) levels, respectively). It can be readily seen that complexation is clearly favorable up to $n = 4$. Complexation

**TABLE 2: Energy Values (kcal/mol), Including ZPVE Corrections, Associated to the Process of Complexation by a CN Ligand in $Ti(NC)_n$ Compounds**

| | B3LYP | CCSD(T) |
|---|---|---|
| $TiNC + CN \rightarrow Ti(NC)_2$ | −105.79 | −104.48 |
| $Ti(NC)_2 + CN \rightarrow Ti(NC)_3$ | −101.55 | −93.85 |
| $Ti(NC)_3 + CN \rightarrow Ti(NC)_4$ | −83.43 | −77.25 |
| $Ti(NC)_4 + CN \rightarrow Ti(NC)_5$ | −5.77 | 3.54 |
| $Ti(NC)_5 + CN \rightarrow Ti(NC)_6$ | −5.73 | −6.47 |

energy is progressively reduced as the number of ligands increases, but the formation of $Ti(NC)_4$ from $Ti(NC)_3$ is still favorable by a large amount, 77 kcal/mol at the CCSD(T) level. This value is substantially reduced when considering the formation of $Ti(NC)_5$, and even at the CCSD(T) level this process is energetically unfavorable. Further complexation up to six ligands is predicted to be only slightly favorable. Extension of the basis set has no significant effect on these complexation energies. For example, the CCSD(T)/6-311+G(2df) values for the formation of $Ti(NC)_2$, $Ti(NC)_3$, and $Ti(NC)_4$ are, respectively, −105.2, −96.58, and −79.47 kcal/mol. These values are very close to those obtained with the 6-311+G(d) basis set (see Table 2). Therefore, according to the results shown in Table 2, it seems that the $Ti(NC)_4$ complex is probably the most favorable from energetic arguments. We may conclude that $Ti(NC)_4$ is a suitable target for experimental observation. Furthermore, its singlet (closed-shell) electronic ground state might confer to this species a certain chemical stability against other reactants.

In view of the results in Table 2 it is certainly clear that $Ti(NC)_4$ should be stable against dissociation of a CN unit. However, this unit is a radical and other dissociation limits can be considered. In particular, it could be illustrative to consider a possible dissociation into a closed-shell species such as $C_2N_2$. We have computed the dissociation into $Ti + 2C_2N_2$, obtaining values of +118.2 and +106.6 kcal/mol at the B3LYP and CCSD(T) levels, respectively. These values seem large enough to support the stability of $Ti(NC)_4$ toward dissociation into cyanogens units. Incidentally, we should mention that we have explored other connectivities within the $[TiC_4N_4]$ potential surface. For example, coordination of Ti to two $C_2N_2$ units produces a species lying about 57 kcal/mol (CCSD(T) level) above $Ti(NC)_4$, whereas the species formed by a $C_2N_2$ unit and two isocyanide ligands lies also 32 kcal/mol (CCSD(T) level) above $Ti(NC)_4$. We have also explored other lower-symmetry structures originated from distortion of the tetrahedral geometry, such as $D_{2d}$, but in all cases the tetrahedral structure was finally reached.

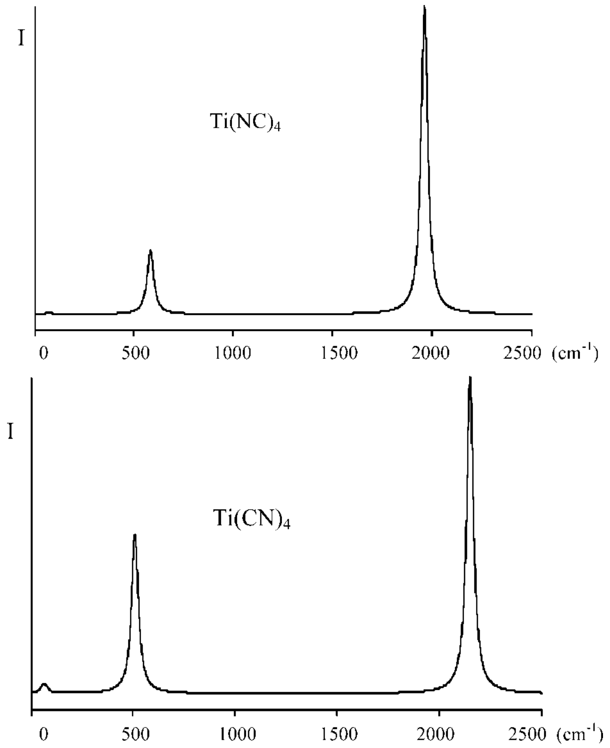

**Figure 3.** Schematic representation of the predicted IR spectra of $Ti(NC)_4$ and $Ti(CN)_4$ complexes. B3LYP/6-311+G(d) vibrational frequencies have been scaled by a factor of 0.9688, according to ref 25.

Given the tetrahedral symmetry of $Ti(NC)_4$, rotational spectroscopy is not the best choice for experimental observation. In order to aid in a possible experimental search for $Ti(NC)_4$ we provide in Figure 3 a simulated IR spectrum employing the B3LYP frequencies. We have scaled the B3LYP/6-311+G(d) frequencies by a scaling factor of 0.9688.[25] The corresponding spectrum of $Ti(CN)_4$ is also shown for comparison. Only normal modes corresponding to $t_2$ symmetry are active in the infrared. The two lines dominating the spectrum of $Ti(NC)_4$ correspond to Ti−N stretching (582 $cm^{-1}$, with the scaling factor of 0.9688) and C−N stretching (1960 $cm^{-1}$), the last one being the most intense one. In the case of the cyanide isomer, $Ti(CN)_4$, a similar profile is obtained, but the C−N stretching is displaced to a somewhat higher value, namely, 2148 $cm^{-1}$, whereas the Ti−C stretching is observed at 508 $cm^{-1}$. These values reflect the slight weakening of C−N bonding in $Ti(NC)_4$ relative to its cyanide counterpart and the slight strengthening of Ti−N bonds compared to Ti−C ones. Vibrational frequencies and IR intensities for the most relevant $Ti(NC)_n$ species are given as Supporting Information.

Our results suggest that $Ti(NC)_4$ might be a plausible target for synthesis. We have carried out analyses of vibrational frequencies, isomerization energies, and stability against different dissociation processes. Therefore, we have followed the suggestions in the recent appeal by Hoffmann et al.[26] on the requirements for reliable predictions of new molecules.

## Conclusions

According to our theoretical predictions, neutral $Ti[CN]_n$ complexes are shown to prefer isocyanide isomers. This preference seems to be mainly related to the larger ability of the CN ligand to back-donate electronic charge to the vacant d orbitals of titanium when it is bonded through the nitrogen atom. The most plausible candidate to experimental detection seems to be $Ti(NC)_4$, a tetrahedral structure with four isocyanide ligands and a closed-shell singlet electronic state. This polyisocyanide structure resembles in its geometrical structure other well-known compounds, such as, for example, $TiCl_4$.

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**Supporting Information Available:** Complete ref 23 and vibrational frequencies and infrared intensities for most relevant

$Ti(NC)_n$ species (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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