A Theoretical Study on the Existence and Structures of Some Hypothetical First-Row Transition-Metal $M$(NCN) Compounds

Maxence Launay and Richard Dronskowski

Institut für Anorganische Chemie der Rheinisch-Westfälischen Technischen Hochschule Aachen, D-52056 Aachen, Germany

Reprint requests to Prof. Dr. R. Dronskowski. E-mail: drons@HAL9000.ac.rwth-aachen.de

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The family of quasi-binary cyanamides/carbodiimides of general formula $M$(NCN) containing divalent 3d transition metals ($M = \text{Mn, Fe, Co, Ni and Cu}$) has been studied by density-functional means; until now, such light transition-metal compounds have not yet been prepared. Twenty-eight structural models have been considered based on known compounds having NCN$^2$− and other triatomic anionic entities (e.g., thiocyanates). After performing LDA geometry optimizations, the relative energetic orderings are interpreted in terms of geometrical factors such as molar volumes and effective coordination numbers; dense structures with octahedral metal coordinations and high-spin electronic configurations are to be expected, especially for the earlier metals (Mn and Fe). Based on GGA total-energy calculations, there is a chance to synthesize these enthalpically unstable compounds, not from the elements but via appropriate exchange reactions employing fairly stable cyanamide/carbodiimide precursors and yielding stable or volatile metal halides which can be removed from the chemical equilibria.

Key words: Light Transition Metals, Cyanamides/Carbodiimides, Geometry Optimization, Density-Functional Theory, Phase Prediction

Introduction

Since the middle of the 1990s, many synthetic and theoretical investigations in cyanamide/carbodiimide chemistry involving the NCN$^2$− complex anion have been carried out. Recently characterized solid cyanamides/carbodiimides contain either alkaline (e.g., Li [1], K [2]) or alkaline-earth (e.g., Mg [3], Ca [4], Sr [3]) metals or main-group (e.g., Si [5], In [6], Pb [7]) elements; in addition, a few of the later transition metals (e.g., Hg [8, 9]) also form compounds that contain NCN$^2$− units.

Nonetheless, neither cyanamides (N≡C−N$^2$−) nor carbodiimides (N=C=N$^2$−) of the lighter transition metals of the 3d block (Mn, Fe, Co...) have been prepared; also, no structure proposals for hypothetical compounds such as MnNCN and FeNCN exist. It is still not clear whether such quasi-binary compounds can be prepared.

In this study, our first major aim is to propose reasonable structural hypotheses for the binary cyanamides/carbodiimides (some of these structures being based on those of $M$(NCN) compounds which have already been characterized) and then try to distinguish the factors favoring or disfavoring certain structures in comparison to others; to do so, we especially focus on the total energies and structural characteristics, namely the molar volume and the effective coordination number. The second main goal of this study is to theoretically calculate whether these still unknown $M$(NCN) materials are thermodynamically stable phases in order to guide the synthetic chemists to decide whether such syntheses should be tried and, if so, under which conditions.

Structural Background

To start with, we consider hypothetical binary $M$(NCN) compounds, with $M$ being one of the five following 3d transition metals: manganese, iron, cobalt, nickel and copper. Then we build structural hypotheses in three different ways:

First, all crystallographic structures which have been determined for the most common cyanamides and carbodiimides are taken into account; that is to say those of alkaline (Li$_2$NCN, $I_4/mmm$, and K$_2$NCN, $C2/m$) and monovalent non-alkaline (Ag$_2$NCN, $P2_1/c$) elements, the ones of alkaline-earth
elements (MgNCN, R3m, and SrNCN, Pnma), those of d10 transition metals (ZnNCN, I42d, HgNCNII, Pbca, and HgNCN(II), P21/c), and finally the one of a main-group element (PbNCN, Pnma).

Second, we consider a couple of other structures containing similar triatomic QCN units, namely the cyanamide ("N"), (thio-/seleno-)cyanates ("S") and chalcogenides ("Q"). The namings are derived from the corresponding parent crystallographic structures of cyanamides ("N"), (thio-/seleno-)cyanates ("S") and chalcogenides ("Q"), respectively, and the related bibliographic references.

### Computational Details

Total-energy calculations and geometry optimizations were performed using the Vienna ab initio Simulation Package (VASP) [11–14] based on density-functional theory. The wave functions were expanded in a plane-wave basis set with kinetic energies below 700 eV. Total energies computed with such a high cut-off value are about 100 meV per formula unit (FU) lower than the ones calculated with a much lower cut-off (300 eV). All the calculations were based on Blochl’s projector augmented wave (PAW) method [15, 16] because, in general, the PAW approach is expected to be more accurate than Vanderbilt’s ultrasoft pseudopotentials [17] for describing the ion-electron interactions; within PAW, an exact valence wave-function is provided in the core region of the electronic orbital.

The integration in the Brillouin zone was done by using the improved tetrahedron method [18] on sets of k points determined using the Monkhorst-Pack scheme [19] (about 8 to 16 k points, depending on the size of the unit cell and the total number of atoms). All the optimizations of atomic coordinates and cell parameters followed a conjugate-gradient minimization of the total energy scheme (Hellmann-Feynman forces on the atoms and stresses on the unit cell [20, 21]). A convergence of total energies quite close to 5 meV/FU was achieved with these parameters.

In general, all atomic positions and unit cell parameters were structurally optimized but the initially given space group symmetry was kept throughout in order to save computing time. Spin-polarization was taken
Table 2. Experimental and optimized cell parameters and C–N bond lengths [Å] for two different M(NCN) compounds: CaNCN (having an ionic character) and PbNCN (having a covalent one). All optimizations are performed by using the PAW approach, with either an LDA or a GGA (Perdew–Wang 91) exchange-correlation functional.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Experimental</th>
<th>Optimized (LDA)</th>
<th>Optimized (GGA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaNCN</td>
<td></td>
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<tr>
<td>Cell parameter $a$</td>
<td>3.595</td>
<td>3.709 [−2.0%]</td>
<td>3.691 [+0.1%]</td>
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<tr>
<td>Cell parameter $c$</td>
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<td>5.470 [−1.6%]</td>
<td>5.395 [+0.7%]</td>
</tr>
<tr>
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<td>1.225(16)</td>
<td>1.229 [+0.3%]</td>
<td>1.236 [+0.9%]</td>
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<tr>
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<td>1.225(16)</td>
<td>1.229 [+0.3%]</td>
<td>1.236 [+0.9%]</td>
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<td>PbNCN</td>
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<tr>
<td>Cell parameter $a$</td>
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<td>3.751 [−3.0%]</td>
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<tr>
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<td>1.297(29)</td>
<td>1.245 [−4.0%]</td>
<td>1.253 [−3.4%]</td>
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</table>

In terms of energetic performances of the LDA and GGA, another test was carried out on the basis of the archetypical and industrially important compound CaNCN [4]. For this highly stable material, reliable thermodynamical data of its standard formation enthalpy is available, corresponding to the formal reaction

$$\text{Ca} + \text{C} + \text{N}_2 \Rightarrow \text{CaNCN}.$$  

The tabulated value for the formation (or reaction) enthalpy $\Delta H_R$ under standard conditions is a strongly exothermic $−350.6$ kJ/mol [24]. When the total electronic energies of all educt (Ca, C, N$_2$) and product (CaNCN) phases are calculated, a theoretical reaction energy at absolute zero – to be compared with the above $\Delta H_R$ assuming negligible enthalpy corrections between 0 and 298 K, a very reasonable approximation – of $−424.7$ kJ/mol is found for the LDA whereas the GGA value is $−359.9$ kJ/mol. Thus, there is an LDA-typical overbinding that largely overestimates the stability of CaNCN by ca. 21%. On the other side, the accuracy of the GGA can be considered very good since, despite also showing a little overbinding, the error is a mere 2.7%. Because of the satisfying GGA result, absolute energetic questions will from now on be considered using the GGA, and the corresponding LDA values are given for illustrative purposes only. With respect to the relative energetic comparisons (i.e., ordering structural alternatives with respect to their total energies), the LDA is considered accurate enough.
Fig. 2(a). Atoms and polyhedra around the transition metal atoms (exhibiting a six-fold coordination) for hypothetical binary \(M(\text{NCN})\) compounds (\(M\) being either Mn, Fe, Co, Ni or Cu) after geometry optimizations of the initial model; in black, white, grey circles: C, N and \(M\) atoms, respectively. Top, from left to right: “N1” (MgNCN), “N2” (orthorhombic SrNCN), “N5” (HgNCN(II)); middle, from left to right: “S2” (orthorhombic AgOCN), “S4” (KSCN), “S8” (monoclinic AgSCN), “S9” (KSeCN) (for \(M =\) Ni or Cu); bottom, from left to right: “Q1” (NiS), “Q3a” (orthorhombic FeS), “Q4” (CoS), “Q5” (CuS), “Q6” (Cr2S6).

Fig. 2(b). Same as before but for five-fold coordination. Top, from left to right: “N4” (HgNCN(I)), “N6” (PbNCN), “N8” (K2NCN), “N9” (Ag2NCN) (for \(M \neq\) Cu); bottom, from left to right: “S5” (orthorhombic AgSCN), “S9” (KSeCN) (for \(M =\) Mn, Fe or Co).

Fig. 2(c). Same as before but for twelve-fold coordination. “Q7” (cubic TiS2).

Fig. 2(d). Same as before but for four-fold coordination. Top, from left to right: “N3” (ZnNCN), “N7” (Li2NCN), “N9” (Ag2NCN) (for \(M =\) Cu); middle, from left to right: “S1” (monoclinic AgOCN), “S3” (hexagonal CuSCN), “S6” (CsSCN), “S7” (orthorhombic CuSCN), “S10” (another hexagonal CuSCN); bottom, from left to right: “Q2a” (tetragonal FeS), “Q2b” (tetragonal FeS), “Q3b” (orthorhombic FeS).

for this purpose; recall that structural parameters come out more accurate using the LDA.

Results

Structure optimizations

Table 3 gives the relative energies for each of the \(M(\text{NCN})\) (with \(M =\) Mn, Fe, Co, Ni, Cu) structural alternatives after structure optimization, and the lowest values are used as references by defining them as energy zeros. Fig. 2 shows the environment of a transition metal atom \(M\) for these \(M(\text{NCN})\) structures obtained by the present approach, while the corresponding lattice parameters and C-N distances are given in Table 4.

We first observe that, quite generally, the computed energy differences regularly decrease from MnNCN to CuNCN; that is to say that structural preferences in terms of differing coordinations are less pronounced while filling up the \(d\) levels. Looked at in greater detail, the most stable structures for transition-metal carbodiimides or cyanamides are derived from the ones of MgNCN (“N1”), SrNCN (“N2”), HgNCN(II) (“N5”), AgOCN (“S2”) and the one parent to NiS (“Q1”) while, at the other end, the ones that are parent to TiS2 (“Q7”), FeS (“Q2a”, “Q2b”), CoS (“Q4”), K2NCN (“N8”) and CsSCN (“S6”) are almost always related to the highest relative energies. Indeed, most of the preferred structures refer to a (more or less distorted) octahedral coordination \(M N_6\) for the transition metal, while a tetrahedral coordination does not seem to be favored. It needs to be stressed that the preference of such a six-fold coordination of nitrogen atoms around these transition metals is quite unexpected; for
Table 3. Differences between the total energies [meV/FU] computed after geometry optimizations of \(M\)(NCN) structures, using an LDA exchange-correlation functional and a spin-polarized approach. Bold: six-fold coordination around each transition metal atom; italic: four-fold coordination; else: five-fold coordination, except for “Q7”: twelve-fold coordination. Among the models giving the lowest total energies: the ones related to \(\text{MgNCN (“N1”), SnNCN (“N2”), HgNCN(II) (“N5”), NiS (“Q1”)}\) and AgOCN (“S2”).

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<td>Q7-6103</td>
<td>Q7-5721</td>
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</tbody>
</table>

Note: energy differences in a range of 10–30 meV/FU (i.e., about 1–3 kJ/mole) are insignificant at this theoretical level.

comparison, we note that the binary MN nitrides, with M being an early transition metal of the 3d row, crystallize in the NaCl type, and those with the later ones (i.e., with \(M = \text{Mn or one of the following metals)}\) crystallize in the zinc blende type with a four-fold metal coordination \([25, 26]\). This finding is especially remarkable considering the fact that the NCN\(^2\^-\) anion is larger than the \(\text{N}^3\^-\) anion, which would favor smaller coordination numbers within an electrostatic/geometric interpretation based on radius ratios.

Table 5 gives the molar volumes of the optimized structures. Surprisingly, most structures are found very dense by the DFT calculations. While the value of the molar volume of an NCN\(^2\^-\) unit is experimentally found at about 28 cm\(^3\)/mol \([10]\), and while the \(M\)(NCN) compounds synthesized to date exhibit molar volumes equal to or higher than 30 cm\(^3\)/mol, the majority of the theoretical values presented here are by far smaller, reflecting dense structures: they range from 18 to 24 cm\(^3\)/mol, in particular the structures which show the lowest relative energies. These densities, decreasing from CuNCN to MnNCN, are found between 22.4 and 22.9 cm\(^3\)/mol for CuNCN, 20.6 and 21.6 cm\(^3\)/mol for NiNCN, 19.4 and 20.1 cm\(^3\)/mol for CoNCN, 18.8 and 19.5 cm\(^3\)/mol for FeNCN, and 18.7 and 20.3 cm\(^3\)/mol for MnNCN, respectively. These data are also plotted in Fig. 3, showing total energies vs. molar volumes for all the \(M\)(NCN) compounds. It is obvious that, especially for the cyanamides/carbodiimides of manganese, iron and cobalt, the denser the structure, the lower the relative energies. For NiNCN and, in particular, CuNCN, this tendency is not so obvious.

In general, high densities are not necessarily related with short interatomic distances but, in the present case, the latter indeed result as relatively short. For the whole series of compounds, the average M-N distances lie between roughly 2.0 and 2.1 Å, which is also a little shorter than what would have been expected from tabulated ionic radii. It may well be the case that a part of this shortening goes back to the DFT-typical “overbonding” despite the good agreement found for the \(\text{C}=\text{N} \) double bonds (see below).

Figure 4 presents correlations of relative energies vs. the effective coordination numbers for all the \(M\)(NCN) compounds; the latter numbers are based on the contribution of Brunner and Schwarzenbach \([27]\). Once again the figures illustrate that a six-fold coordination slightly favors the stability of \(M\)(NCN) compounds as compared to a four-fold coordination. Summarizing, it appears that a rather high density (compared to the known cyanamides and carbodiimides) in combination with an octahedral coordination around the transition metal atoms are decisive characteristics of the most stable structures.

Another point worthwhile investigating is the structural difference between cyanamides and carbodiimides in this group of light transition-metal \(M\)(NCN) compounds. Within our calculations, we can observe that among the five structures found as the most stable ones, four of them (namely “N1”, “N2”, “N5” and “Q1”) exhibit two C-N bonds in their NCN\(^2\-) part of this shortening goes back to the DFT-typical “overbonding” despite the good agreement found for the \(\text{C}=\text{N} \) double bonds (see below).
Table 4. Cell parameters and C–N bond lengths obtained after structural optimizations using an LDA exchange-correlation functional and a spin-polarized approach. If not specified, all angles of the unit cell are equal to 90°.

<table>
<thead>
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AgOCN) shows two rather different C-N bond lengths (1.20 Å and 1.27 Å); this structural type, with an asymmetrical N≡C-N2 unit, qualifies as a cyanamide. Nonetheless, one has to be very careful to discriminate between carbodiimide and cyanamide isomers based upon results that were obtained with a DFT method; very recently, it has been shown that DFT methods fail to correctly reproduce the relative stabilities of cyanamides and carbodiimides, because they tend to systematically overestimate the stability of the carbodiimide isomers [28]. A closer analysis based on correlated (MP2 and QCISD) quantum-chemical calculations on smaller model systems also shows [28] that the DFT problem is largely independent from the used exchange-correlation functional and, quite important, from the nature of the atoms which coordinate the NCN2− unit. The error scales linearly with the system size and, once again, demonstrates the DFT-typical tendency for a homogenization of the electronic density.

On the other side, there is an empirical correlation [7] derived from the Pearson hardnesses η of the metals which induce either the cyanamide (“soft” atom) or the carbodiimide (“hard” atom) shape. Ca2+ and Sr2+ cations are “hard” ions with large η values (19.5 eV and 16.3 eV, respectively [29]) and predominantly ionic bonding to the NCN2− units; as a consequence, CaNCN and SrNCN are carbodiimides (see Fig. 1, left). On the contrary, Ag+ and Hg2+ and Pb2+ cations are “soft” ions as their hardnesses are equal to 7.0, 7.7 and 8.5 eV, respectively [29], and there is covalent bonding to one side of the NCN2− unit; as a result, Ag2NCN, PbNCN (see Fig. 1, right) and HgNCN(II) can be referred to as cyanamides. Although the five transition metal cations considered here can also be considered as “soft” ions (η = 9.0 eV for
Mn$^{2+}$, 7.2 eV for Fe$^{2+}$, 8.2 eV for Co$^{2+}$, 8.5 eV for Ni$^{2+}$, and 8.3 eV for Cu$^{2+}$ [29]), which would favor the cyanamide shape, they appear to form carbodiimides according to the geometry optimizations (see above). If this must be taken seriously, it is the first breakdown of the before-mentioned shape rule, and this exciting finding is presumably related to the spin-polarized electronic configurations of the transition-metal ions; all known cyanamides and carbodiimides are diamagnetic.

Quite generally, spin-polarization plays a decisive role for lowering the total energies. Without going too much into the details, we note that the most stable structures found (e.g., “Q1”, “N2”, “N5”) are the ones that are characterized by high-spin electronic configurations. For the exemplary case of MnNCN, one finds five unpaired electrons ($t_{2g}^3$, $e_g^2$) and an antiferromagnetic coupling between the Mn$^{2+}$ centers. For the less favorable structural models, ferromagnetically coupled low-spin configurations are also found. Whenever the coordination environment deviates substantially from a regular one (e.g., strongly distorted octahedral configuration), intermediate spin moments are detected, too.

**Thermochemistry**

In this part, we focus on possible synthetic pathways to the quasi-binary transition-metal cyanamides and carbodiimides starting from the elements. Alternatively, the decay of these compounds into the elements or nitrides/carbides is investigated in terms of enthalpic and entropic criteria (see below). This is intended as a starting point for synthetic chemists searching for M(NCN) compounds. To do so, data for all competing MN, MC and M$_2$C phases were taken from the crystallographic data bases; if corresponding entries were not available, hypothetical nitrides/carbides were nonetheless considered, and their structures were optimized starting with those of FeN and CoN ($F\bar{4}3m$) [30, 31].
As introduced in the theoretical section, calculated reaction energies – expected to be very close to the actual reaction enthalpies $\Delta H_R$ – arrive as the difference between the total electronic energies of the products and those of the educts. Before going into the numerical details, we mention that all reactions involve gaseous species (C$_2$N$_2$, N$_2$) as educts, having important implications for the Gibbs energies $\Delta G_R$: If cyanoamides/carbonediimides are to be sought for, high-temperature routes should be avoided at all costs because there is an entropic destabilization of cyanoamide/carbonodiimide compounds due to the $T \Delta S$ stabilization of the gaseous educts. For low temperatures, however, let us neglect the entropic term and concentrate on the enthalpies only.

Table 6 gives the corresponding GGA and, for comparison, LDA energy values computed for the six reactions. For reaction #4, most of the GGA reaction energies are found positive (three cases: $M = \text{Fe, Co or Ni}$), showing that obtaining cyanoamides/carbonediimides starting from M$_2$C carbides is not an enthalpically reasonable choice. On the contrary, all the computed GGA reaction energies for reactions #2, 3, 5 and 6 are found negative: thus, educt phases involving $M$C carbides or/and MN nitrides appear as more attractive candidates but they would require unfavorably high temperatures keeping in mind the inertness of these solid phases (see above). We also emphasize that several of the binary transition-metal compounds of the type $M_2C$, $MC$, $MN$ have not yet been reported in the literature. Finally, the direct route (reaction #1) starting with the elements evidences all GGA reaction energies as positive such that, very unfortunately from a synthetic point of view, all five $M$(CN) compounds are predicted as enthalpically unstable with respect to the elements. Reconsidering the above-mentioned stabilization of the gaseous educt $N_2$, the hypothetical phases $M$(NCN) are thermodynamically unstable – and even more so – in terms of $\Delta G_R$.

Table 6 also shows that the trends obtained from the GGA and the (energetically less accurate) LDA calculations are about the same, and there is an (expected) LDA-typical overestimation of cyanamide/carbonediimide stability on the order of 70 kJ/mol, just like for the preceding test case of CaNCN (see section on computational details). Moreover, if we focus on reaction #1, both approaches reveal an increasing destabilization of the $M$(NCN) phases with respect to the elements when moving to the late 3d elements (see Fig. 5); this evolution of the relative stabilities is re-


<table>
<thead>
<tr>
<th>MnNCN</th>
<th>FeNCN</th>
<th>CoNCN</th>
<th>NiNCN</th>
<th>CuNCN</th>
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</tr>
</tbody>
</table>

VC ($Fm\bar{3}m$) [32], Fe$_3$C and Co$_2$C ($Pnnm$) [33, 34], respectively.

Geometry optimizations were performed as described before and the total energy values used for the calculations of the chemical reactions energies were the ones corresponding to the optimized structures. The six hypothetical chemical reactions considered are as follows:

$\text{#1: } M + C + N_2 \Rightarrow \text{MNCN}$

$\text{#2: } M + 2C \Rightarrow \text{MNCN}$

$\text{#3: } M + N + \frac{1}{2}C_2N_2 \Rightarrow \text{MNCN}$

$\text{#4: } \frac{1}{2}M_2C + \frac{1}{2}C_2N_2 + \frac{1}{4}N_2 \Rightarrow \text{MNCN}$

$\text{#5: } \frac{1}{2}MN + \frac{1}{2}MC + \frac{1}{2}C_2N_2 + \frac{1}{2}N_2 \Rightarrow \text{MNCN} \text{ (i.e., } \frac{1}{2}\#2 + \frac{1}{4}\#3)$

$\text{#6: } \frac{3}{2}MN + \frac{1}{2}MC + \frac{1}{2}C_2N_2 + \frac{1}{2}N_2 \Rightarrow \text{MNCN} \text{ (i.e., } \frac{3}{2}\#2 + \frac{1}{4}\#3)$
bonded, Ni₃C (+68 kJ/mol), FeS (+102 kJ/mol), CuN₃
(+252 kJ/mol), Pb(N₃)₂ (+437 kJ/mol), and CoSO₄
(+888 kJ/mol) [24]; obviously, the positive forma-
tion enthalpies predicted for M(NCN) are not exceed-
ingly high. Nonetheless, it is clear that the synthesis of
M(NCN) will be unsuccessful if the elements are used
as eucts; therefore, alternative strategies need to be
sought for. For example, a metathesis such as

$$MX_2 + A(NCN) \Rightarrow M(NCN) + AX_2$$

in which A(NCN) symbolizes a not exceedingly sta-
ble cyanamide/carbodiimide and AX₂ is an exception-
ally stable halide – probably highly volatile such that
it can be removed from the equilibrium – appears to be
a reasonable starting point; low-temperature routes are
nonetheless needed. Corresponding synthetic research
is under way in our own laboratories.

**Conclusion**

Density-functional total-energy calculations have
been performed to optimize twenty-eight structural
hypotheses for quasi-binary transition-metal cyanamides/carbodiimides M(NCN) (M being either
Mn, Fe, Co, Ni, or Cu), which have not yet been pre-
pared. The most favorable structures are characterized
by octahedral coordinations and a high-spin electronic
configuration of the metal atoms, especially for the
compounds containing Mn and Fe, the latter atoms
being preferentially coupled antiferromagnetically. All
compounds are predicted as enthalpically unstable ma-
terials; Nonetheless, their syntheses are proposed for
the elements but through exchange reactions at relatively low
temperatures.
Acknowledgements

The authors thank Dr. Xiaohui Liu for fruitful scientific discussions about the cyanamide family of compounds, Dr. Bernhard Eck for computational help, and the computing center (RZ) of RWTH Aachen for providing computer time. One of the authors (M. L.) also thanks the generous financial support of the Alexander von Humboldt Foundation for this research work.

Note added in proof: We have succeeded in making pure MnNCN, a carbodiimide by structure. The green crystals are isotypical with CaNCN (hexagonal system) and contain octahedrally coordinated and antiferromagnetically coupled high-spin Mn$^{2+}$ ions, as predicted.