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

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The family of quasi-binary cyanamides/carbodiimides of general formula M(NCN) containing divalent $3d$ transition metals (M = 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 tri-atomic 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 ($N{\equiv}C{-}N^{2-}$) 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 distin-guish 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, *I4/mmm*, and K$_2$NCN, *C2/m*) and monovalent non-alkaline (Ag$_2$NCN, *P2$_1$/c*) elements, the ones of alkaline-earth

Table 1. Correspondences between hypothetical structures for binary transition metal cyanamides and some experimental structures for cyanamides, (thio/seleno-)cyanates and chalcogenides.

M(NCN) label	Formula of the parent compound	Corre- sponding space group	N Atoms around M (after opti- mization)	ICSD reference of the parent compound	Reference for the parent compound
"N1"	MgNCN	$R\bar{3}m$	6	75039	[3]
"N2"	SrNCN	$Pnma$	6	75040	[3]
"N3"	ZnNCN	$I\bar{4}2d$	4	280523	[35]
"N4"	HgNCN(I)	$Pbca$	5	411067	[8]
"N5"	HgNCN(II)	$P2_1/c$	6	412278	[9]
"N6"	PbNCN	$Pnma$	5	410915	[7]
"N7"	Li$_2$NCN	$I4/mmm$	4	200369	[1]
"N8"	K$_2$NCN	$C2/m$	5	411094	[2]
"N9"	Ag$_2$NCN	$P2_1/c$	5 or 4*	411091	[36]
"S1"	AgOCN	$P2_1/m$	4	18149	[37]
"S2"	AgOCN	$Cmcm$	6	30516	[38]
"S3"	CuSCN	$P6_3mc$	4	32578	[39]
"S4"	KSCN	$Pbcm$	6	36073	[40]
"S5"	AgSCN	$Pnnm$	5	201359	[41]
"S6"	CsSCN	$Pnma$	4	60523	[42]
"S7"	CuSCN	$Pbca$	4	124	[43]
"S8"	AgSCN	$C2/c$	6	16668	[44]
"S9"	KSeCN	$P2_1/c$	5 or 6**	23951	[45]
"S10"	CuSCN	$R3m$	4	24372	[46]
"Q1"	NiS	$P6_3/mmc$	6	76683	[47]
"Q2" a/b†	FeS	$P4/nnm$	4(a) / 4(b)	81087	[48]
"Q3" a/b†	FeS	$Pnma$	6(a) / 4(b)	35009	[49]
"Q4"	CoS	$Pa\bar{3}$	6	86351	[50]
"Q5"	CuS	$P6_3/mmc$	6	61793	[51]
"Q6"	Cr$_5$S$_6$	$P\bar{3}c1$	6	43044	[52]
"Q7"	TiS$_2$	$Fd\bar{3}m$	12	72042	[53]

* 5 for MnNCN, FeNCN, CoNCN & NiNCN; 4 for CuNCN. ** 5 for MnNCN, FeNCN & CoNCN; 6 for NiNCN & CuNCN. † For each structure M(NCN) parent to FeS: two possibilities, according to the orientation of NCN^{2-} units.

elements (MgNCN, $R\bar{3}m$, and SrNCN, $Pnma$), those of d^{10} transition metals (ZnNCN, $I\bar{4}2d$, HgNCN(I), $Pbca$, and HgNCN(II), $P2_1/c$), 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 cyanate (OCN$^-$), thiocyanate (SCN$^-$), and seleno-cyanate (SeCN$^-$) anions. Thus, structural candidates are derived from AgOCN ((1) $P2_1/m$ and (2) $Cmcm$) for the cyanates group – the structure of NaOCN is equivalent to the one of MgNCN –, KSCN ($Pbcm$), CsSCN ($Pnma$), CuSCN ((1) $P6_3mc$, (2) $Pbca$ and (3) $R3m$) and AgSCN ((1) $Pnnm$ and (2) $C2/c$) for the thio-cyanates group – the structure of NaSCN is very similar to the one of SrNCN –, and KSeCN ($P2_1/c$) as the only selenocyanate.

Third, structural starting points are generated from the crystal structures of transition-metal chalcogenides

(MQ_x compounds, with 1 or 2 being the most common values for x), where chalcogens are replaced by NCN^{2-} units: FeS ((1) $P4/nnm$ and (2) $Pnma$), CoS ($Pa\bar{3}$), NiS ($P6_3/mmc$), CuS ($P6_3/mmc$), Cr$_5$S$_6$ ($P\bar{3}c1$) and TiS$_2$ ($Fd\bar{3}m$). The reason for proposing such structural models is that the equally charged cyanamide group NCN^{2-} exhibits a volume increment which is very close to the one of the sulfide S^{2-} anion: the values are 28 and 29 cm^3/mol, respectively [10].

Table 1 gives an overview of all M(NCN) structural models ("N1" to "N9", "S1" to "S10", "Q1" to "Q7"), their namings being 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 Blöchl's projector augmented wave (PAW) method [15, 16] because, in general, the PAW approach is expected to be more accurate than Vanderbilt ultra-soft pseudo-potentials [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.

| CaNCN (space group: $R\bar{3}m$)	Experimental [4]	Optimized (LDA)	Optimized (GGA)
Cell parameter a	3.695	3.598 [−2.6%]	3.697 [+0.1%]
Cell parameter c	14.709	14.547 [−1.1%]	14.768 [+0.4%]
Short C–N distance	1.225(16)	1.229 [+0.3%]	1.236 [+0.9%]
Long C–N distance	1.225(16)	1.229 [+0.3%]	1.236 [+0.9%]
PbNCN (space group: $Pnma$)	Experimental [7]	Optimized (LDA)	Optimized (GGA)
Cell parameter a	5.557	5.470 [−1.6%]	5.595 [+0.7%]
Cell parameter b	3.868	3.751 [−3.0%]	3.828 [−1.0%]
Cell parameter c	11.735	11.612 [−1.0%]	11.892 [+1.3%]
Short C–N distance	1.156(28)	1.205 [+4.2%]	1.229 [+6.3%]
Long C–N distance	1.297(29)	1.245 [−4.0%]	1.253 [−3.4%]
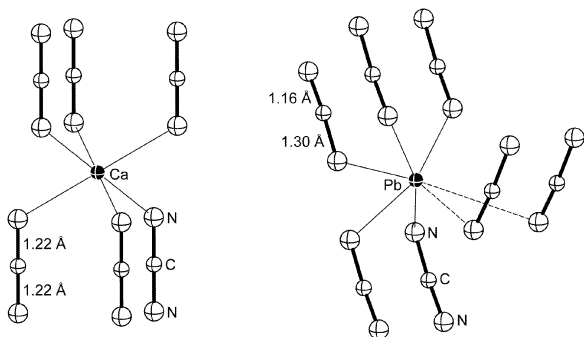
Fig. 1. Cuts from the crystal structures of a carbodiimide phase, CaNCN (left), and a cyanamide phase, PbNCN (right); data taken from [4] and [7].

into account in order to provide the best description of the electron-electron interactions; as a consequence, the corresponding values of the total energies are significantly lower than those extracted from non spin-polarized calculations: differences are about (or even higher than) 100 meV/FU.

In order to determine whether the local-density approximation (LDA) or the generalized-gradient approximation (GGA, namely the Perdew-Wang 91 model [22, 23]) is better suited to deal with the computational problem, we first ran geometry optimization tests for two existing compounds: a more ionic one, the carbodiimide CaNCN [4], and a more covalent one, the cyanamide PbNCN [7]. A sketch of the two structures is given in Fig. 1. Table 2 offers the experimental and optimized cell parameters, and also the corresponding C-N bond lengths. With these results, one can easily see that *both* LDA and GGA approaches yield accept-

able lattice parameters (with a slight underestimation, LDA, and overestimation, GGA, of the cell parameters, but such tendencies are typical for these DFT methods); both strategies, however, are not fully satisfactory with respect to the anionic C-N distances: The case of PbNCN clearly highlights that both types of exchange-correlation functionals tend to *homogenize* electron densities in such a way that the C-N bond lengths are not reproduced very well, making the cyanamide Pb-NCN (one single C-N bond and one triple C≡N bond) almost look like a carbodiimide with two C=N double bonds (see also below); in this respect, the results obtained within the GGA approach are considered *worse* than the ones from LDA. The superior performance of the LDA functional – in terms of structural parameters only! – probably goes back to a fortunate error cancellation, and we therefore decided to rely on the LDA functional *only* for the geometry optimizations of the M(NCN) structural models.

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

$$Ca + C + N_2 \Rightarrow CaNCN.$$
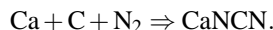
The tabulated value for the formation (or reaction) enthalpy ΔH_R under standard conditions is a strongly exothermic −350.6 kJ/mol [24]. When the total electronic energies of all educt (Ca, C, N_2) and product (CaNCN) phases are calculated, a theoretical reaction energy at absolute zero – to be compared with the above ΔH_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.* 21.1%. 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
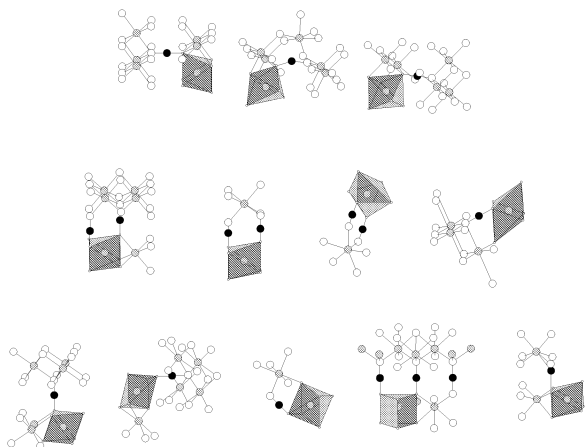
Fig. 2(a). Atoms and polyhedra around the transition metal atoms (exhibiting a *six*-fold coordination) for hypothetical binary M(NCN) compounds (M being either Mn, Fe, Co, Ni or Cu) after geometry optimizations of the initial model; in black, white, grey circles: C, N and M atoms, respectively. Top, 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" (Cr$_5$S$_6$).
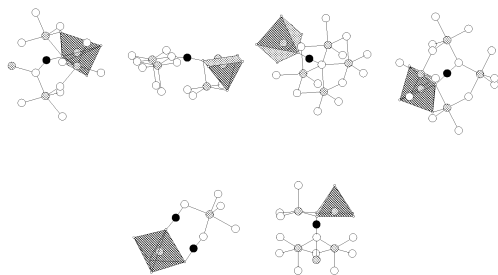

Fig. 2(b). Same as before but for *five*-fold coordination. Top, from left to right: "N4" (HgNCN(I)), "N6" (PbNCN), "N8" (K$_2$NCN), "N9" (Ag$_2$NCN) (for $M \neq$ Cu); bottom, from left to right: "S5" (orthorhombic AgSCN), "S9" (KSeCN) (for M = Mn, Fe or Co).

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(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(NCN) structures obtained
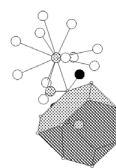

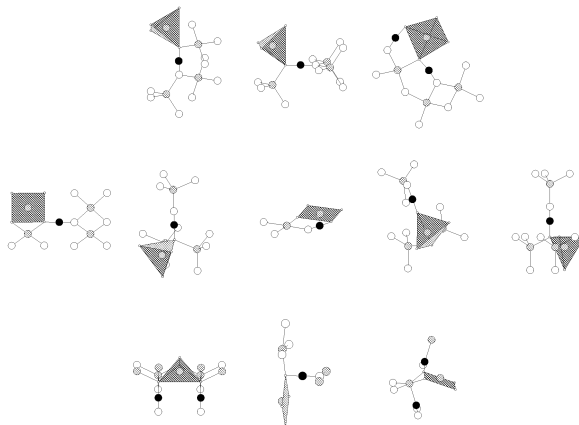Fig. 2(c). Same as before but for *twelve*-fold coordination. "Q7" (cubic TiS$_2$).

Fig. 2(d). Same as before but for *four*-fold coordination. Top, from left to right: "N3" (ZnNCN), "N7" (Li$_2$NCN), "N9" (Ag$_2$NCN) (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).

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 TiS$_2$ ("Q7"), FeS ("Q2a", "Q2b"), CoS ("Q4"), K$_2$NCN ("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 MN$_6$ 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 MgNCN ("N1"), SrNCN ("N2"), HgNCN(II) ("N5"), NiS ("Q1") and AgOCN ("S2").

MnNCN	FeNCN	CoNCN	NiNCN	CuNCN
Q1–0000	**Q1–0000**	**Q1–0000**	**Q1–0000**	*N3–0000*
N2–0042	**N2–0082**	**N1–0116**	**N1–0050**	*N7–0054*
N1–0224	**N1–0140**	**N5–0178**	**N5–0057**	**N5–0090**
N5–0224	*Q3a–0142*	**S2–0219**	N6–0181	**N1–0103**
Q3a–0259	**S2–0163**	*Q3a–0305*	*Q3b–0183*	**Q1–0143**
Q5–0275	**N5–0232**	**N2–0403**	*N3–0208*	*S3–0179*
S2–0290	*N3–0355*	*N3–0430*	*S1–0216*	*S10–0196*
S10–0401	N4–0398	*S10–0502*	**S2–0219**	**N2–0205**
N4–0522	*S10–0406*	N6–0502	**N2–0262**	N6–0226
N6–0546	N6–0463	*N7–0503*	**S9–0281**	**S9–0242**
S1–0561	**Q5–0490**	*S3–0546*	N7–0314	N9–0252
Q3b–0564	*Q3b–0548*	S9–0668	**Q3a–0333**	**S8–0297**
S9–0599	*S1–0604*	*S1–0670*	*S3–0390*	N4–0319
S8–0732	S9–0608	**S8–0680**	*S10–0397*	**S2–0391**
N3–0776	N7–0731	S5–0756	S5–0519	**S4–0402**
N7–0852	S3–0785	N4–0780	**S8–0544**	S5–0406
N9–0856	*S7–0801*	*Q3b–0840*	N4–0606	*S7–0416*
S5–0866	**S8–0809**	**Q5–0869**	N9–0615	*S1–0419*
S7–0919	S5–0829	*S7–0915*	*S7–0665*	*S6–0481*
S3–0934	N8–0895	N9–0928	*S6–0751*	**Q3a–0482**
Q6–1019	N9–0898	**Q4–0983**	**Q5–0830**	N8–0617
S4–1113	**Q4–0924**	N8–1058	**Q4–0842**	**Q4–0634**
N8–1134	**S4–1119**	**S4–1134**	**S4–0903**	*Q3b–0637*
S6–1138	**Q6–1153**	*S6–1137*	*Q2b–0991*	**Q5–0701**
Q4–1214	*S6–1221*	**Q6–1548**	N8–1255	*Q2b–0990*
Q2b–1595	*Q2a–1635*	*Q2b–1597*	**Q6–1632**	*Q2a–1487*
Q2a–1958	*Q2b–1800*	*Q2a–1890*	*Q2a–1790*	**Q6–1541**
Q7–6009	Q7–5884	Q7–6103	Q7–5721	Q7–4850

Note: energy differences in a range of $10-30$ meV/FU (*i. e.*, about $1-3$ kJ per 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 = 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 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 C=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-} units having quite the same length (about 1.22 Å to 1.24 Å, see Table 4); these may therefore be called *carbodiimide* compounds, referring to N=C=N^{2-} units. On the opposite, the fifth structure ("S2", derived from

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°.

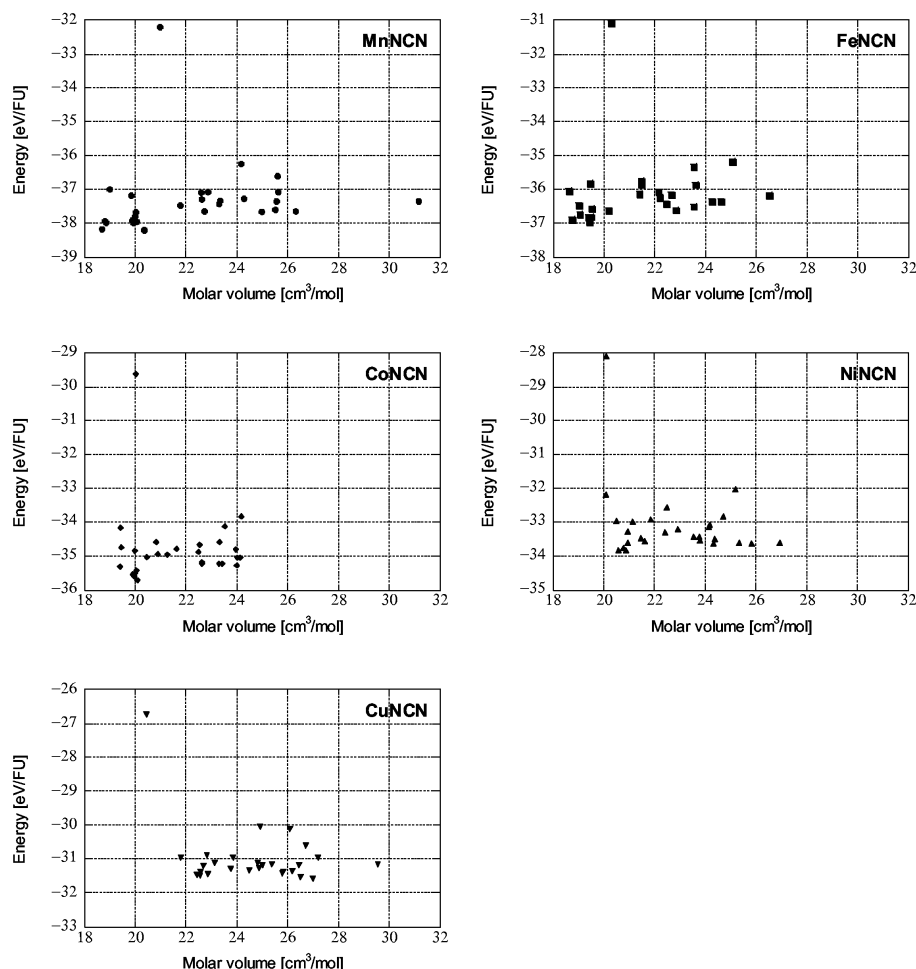|	Space group	Z	a [Å]	b [Å]	c [Å]	β or γ Angle [°]	C–N Bond Length [Å]	N–C–N Angle [°]
MnNCN:								
"N1"	$R\bar{3}m$	3	2.806	2.806	14.550	120	1.24	180.00
"N2"	$Pnma$	4	9.022	2.696	5.105	–	1.26, 1.30	154.30
"N3"	$I\bar{4}2d$	8	7.431	7.431	5.605	–	1.24	172.62
"N4"	$Pbca$	8	10.125	4.673	5.622	–	1.28, 1.30	142.75
"N5"	$P2_1/c$	4	5.188	5.396	4.718	108.53	1.24	180.00
"N6"	$Pnma$	4	5.121	2.800	11.574	–	1.22, 1.24	174.19
"N7"	$I\bar{4}m2$	2	3.258	3.258	9.751	–	1.23	180.00
"N8"	Cm	2	4.001	3.976	4.899	102.96	1.20, 1.31	168.68
"N9"	$P2_1/c$	4	5.401	5.593	6.121	113.31	1.23, 1.24	179.12
"S1"	$P2_1/m$	2	5.094	5.658	3.034	87.35	1.22, 1.23	179.35
"S2"	$Cmcm$	4	2.785	9.695	4.889	–	1.20, 1.28	180.00
"S3"	$P6_3mc$	2	3.147	3.147	9.404	120	1.19, 1.34	180.00
"S4"	$Pbcm$	4	6.011	4.663	5.353	–	1.23, 1.26	162.89
"S5"	$Pnnm$	4	5.373	9.763	2.956	–	1.20, 1.26	173.99
"S6"	$Pnma$	4	5.617	5.496	5.512	–	1.22, 1.24	179.56
"S7"	$Pbca$	8	9.405	5.442	5.868	–	1.21, 1.33	153.13
"S8"	$C2/c$	8	8.995	5.580	11.016	148.48	1.21, 1.25	175.27
"S9"	$P2_1/c$	4	2.800	6.723	9.007	90.37	1.22, 1.24	177.50
"S10"	$R3m$	6	2.716	2.716	31.189	120	1.16, 1.27	180.00
"Q1"	$P6_3/mmc$	2	2.854	2.854	9.575	120	1.24	180.00
"Q2a"	$P4/nmm$	2	3.501	3.501	6.547	–	1.17, 1.32	180.00
"Q2b"	$P4/nmm$	2	3.844	3.844	5.755	–	1.25	180.00
"Q3a"	$Pnma$	4	4.872	2.806	9.745	–	1.20, 1.28	179.78
"Q3b"	$Pnma$	4	5.013	4.863	6.187	–	1.30, 1.31	126.34
"Q4"	$Pa\bar{3}$	4	5.015	5.015	5.015	–	1.25	180.00
"Q5"	$P6_3/mmc$	4	2.693	2.693	19.869	120.00	1.25	180.00
"Q6"	$P\bar{3}c1$	12	6.820	6.820	9.808	120.00	1.32, 1.33	125.49
"Q7"	$Fd\bar{3}m$	8	6.530	6.530	6.530	–	1.41	109.47
FeNCN:								
"N1"	$R\bar{3}m$	3	2.782	2.782	14.405	120	1.24	180.00
"N2"	$Pnma$	4	8.955	2.794	4.997	–	1.25, 1.29	157.42
"N3"	$I\bar{4}2d$	8	7.438	7.438	5.484	–	1.24	177.18
"N4"	$Pbca$	8	10.020	4.622	5.603	–	1.27, 1.29	144.38
"N5"	$P2_1/c$	4	5.070	5.513	4.792	109.13	1.24	180.00
"N6"	$Pnma$	4	5.111	2.696	11.342	–	1.22, 1.25	174.04
"N7"	$I\bar{4}m2$	2	2.731	2.731	9.888	–	1.23	180.00
"N8"	Cm	2	3.833	3.918	5.175	108.83	1.18, 1.31	178.95
"N9"	$P2_1/c$	4	5.174	5.311	6.273	113.99	1.23, 1.26	173.91
"S1"	$P2_1/m$	2	5.100	5.281	2.993	88.07	1.22, 1.23	178.89
"S2"	$Cmcm$	4	2.779	9.583	4.858	–	1.20, 1.28	180.00
"S3"	$P6_3mc$	2	3.155	3.155	10.217	120	1.18, 1.28	180.00
"S4"	$Pbcm$	4	6.054	4.577	5.149	–	1.22, 1.28	153.43
"S5"	$Pnnm$	4	5.160	9.778	2.816	–	1.21, 1.26	165.84
"S6"	$Pnma$	4	5.518	5.314	4.870	–	1.23, 1.24	179.56
"S7"	$Pbca$	8	10.510	5.205	5.503	–	1.18, 1.29	177.28
"S8"	$C2/c$	8	8.864	5.611	10.737	149.29	1.22, 1.25	172.50
"S9"	$P2_1/c$	4	2.750	6.698	8.876	90.92	1.22, 1.25	174.11
"S10"	$R3m$	6	2.781	2.781	31.518	120	1.18, 1.30	180.00
"Q1"	$P6_3/mmc$	2	2.804	2.804	9.474	120	1.23, 1.24	180.00
"Q2a"	$P4/nmm$	2	3.468	3.468	6.502	–	1.16, 1.33	180.00
"Q2b"	$P4/nmm$	2	3.824	3.824	5.693	–	1.25	180.00
"Q3a"	$Pnma$	4	4.821	2.851	9.516	–	1.20, 1.28	179.49
"Q3b"	$Pnma$	4	5.020	4.817	6.163	–	1.30, 1.31	127.74
"Q4"	$Pa\bar{3}$	4	4.982	4.982	4.982	–	1.24	180.00
"Q5"	$P6_3/mmc$	4	2.729	2.729	19.585	120	1.24	180.00
"Q6"	$P\bar{3}c1$	12	6.798	6.798	9.693	120	1.30, 1.34	128.05
"Q7"	$Fd\bar{3}m$	8	6.460	6.460	6.460	–	1.40	109.47
CoNCN:								
"N1"	$R\bar{3}m$	3	2.883	2.883	13.811	120	1.24	180.00
"N2"	$Pnma$	4	9.096	2.907	4.877	–	1.24, 1.26	166.74
"N3"	$I\bar{4}2d$	8	7.684	7.684	5.401	–	1.23, 1.24	175.89
"N4"	$Pbca$	8	9.871	4.586	6.130	–	1.27, 1.28	147.74
"N5"	$P2_1/c$	4	4.922	5.778	4.969	110.70	1.24	180.00
"N6"	$Pnma$	4	4.955	2.779	11.298	–	1.22, 1.24	169.62
"N7"	$I\bar{4}m2$	2	2.811	2.811	9.793	–	1.23	180.00
"N8"	Cm	2	3.872	3.989	5.182	110.72	1.18, 1.30	178.99
"N9"	$P2_1/c$	4	5.100	5.192	6.098	117.22	1.22, 1.25	178.45
"S1"	$P2_1/m$	2	5.030	5.307	2.989	88.09	1.22, 1.23	178.89
"S2"	$Cmcm$	4	2.859	9.441	4.921	–	1.19, 1.28	180.00
"S3"	$P6_3mc$	2	2.889	2.889	10.392	120	1.18, 1.29	180.00
"S4"	$Pbcm$	4	5.978	4.619	5.008	–	1.22, 1.28	151.84
"S5"	$Pnnm$	4	5.141	9.735	2.820	–	1.20, 1.26	171.77
CoNCN:								
"S6"	$Pnma$	4	5.219	5.930	5.005	–	1.22, 1.23	179.89
"S7"	$Pbca$	8	10.090	5.593	5.638	–	1.18, 1.29	177.43
"S8"	$C2/c$	8	8.571	5.488	10.724	147.40	1.20, 1.26	173.88
"S9"	$P2_1/c$	4	2.799	6.592	8.692	90.75	1.22, 1.24	173.06
"S10"	$R3m$	6	2.898	2.898	30.989	120	1.18, 1.31	180.00
"Q1"	$P6_3/mmc$	2	2.904	2.904	9.132	120	1.23, 1.24	180.00
"Q2a"	$P4/nmm$	2	3.515	3.515	6.500	–	1.17, 1.31	180.00
"Q2b"	$P4/nmm$	2	3.742	3.742	5.575	–	1.24	180.00
"Q3a"	$Pnma$	4	4.779	2.968	9.390	–	1.19, 1.28	179.27
"Q3b"	$Pnma$	4	5.147	4.886	5.939	–	1.27, 1.28	141.33
"Q4"	$Pa\bar{3}$	4	5.055	5.055	5.055	–	1.23	180.00
"Q5"	$P6_3/mmc$	4	2.792	2.792	19.663	120	1.25	180.00
"Q6"	$P\bar{3}c1$	12	6.690	6.690	9.993	120	1.29, 1.32	134.68
"Q7"	$Fd\bar{3}m$	8	6.430	6.430	6.430	–	1.39	109.47
NiNCN:								
"N1"	$R\bar{3}m$	3	2.927	2.927	13.822	120	1.24	180.00
"N2"	$Pnma$	4		2.859	4.758	–	1.23, 1.24	179.19
"N3"	$I\bar{4}2d$	8	7.946	7.946	5.329	–	1.23	175.08
"N4"	$Pbca$	8	9.551	5.212	6.117	–	1.22, 1.24	177.12
"N5"	$P2_1/c$	4	4.922	5.949	5.060	111.35	1.24	180.00
"N6"	$Pnma$	4	4.917	2.805	11.714	–	1.22, 1.24	176.36
"N7"	$I\bar{4}m2$	2	2.899	2.899	9.625	–	1.23	180.00
"N8"	Cm	2	4.045	4.018	4.753	104.76	1.19, 1.30	179.63
"N9"	$P2_1/c$	4	5.168	5.245	6.113	116.11	1.22, 1.24	175.93
"S1"	$P2_1/m$	2	4.943	5.354	3.385	87.22	1.22, 1.23	176.81
"S2"	$Cmcm$	4	2.933	9.456	5.016	–	1.20, 1.27	180.00
"S3"	$P6_3mc$	2	2.957	2.957	10.320	120	1.18, 1.29	180.00
"S4"	$Pbcm$	4	6.173	4.556	5.162	–	1.22, 1.27	159.85
"S5"	$Pnnm$	4	5.428	9.396	2.919	–	1.20, 1.25	171.29
"S6"	$Pnma$	4	5.196	6.007	5.146	–	1.22, 1.23	179.97
"S7"	$Pbca$	8	10.271	5.515	5.496	–	1.18, 1.29	178.39
"S8"	$C2/c$	8	8.826	5.582	10.691	148.11	1.21, 1.26	172.65
"S9"	$P2_1/c$	4	2.763	6.343	8.999	89.81	1.22, 1.24	179.46
"S10"	$R3m$	6	2.978	2.978	30.285	120	1.18, 1.28	180.00
"Q1"	$P6_3/mmc$	2	2.974	2.974	9.047	120	1.23, 1.24	180.00
"Q2a"	$P4/nmm$	2	3.574	3.574	6.547	–	1.18, 1.30	180.00
"Q2b"	$P4/nmm$	2	3.753	3.753	5.826	–	1.24	180.00
"Q3a"	$Pnma$	4	4.916	3.090	9.384	–	1.20, 1.27	179.55
"Q3b"	$Pnma$	4	5.072	4.966	6.809	–	1.22, 1.23	176.76
"Q4"	$Pa\bar{3}$	4	5.145	5.145	5.145	–	1.23	180.00
"Q5"	$P6_3/mmc$	4	2.874	2.874	19.617	120	1.24	180.00
"Q6"	$P\bar{3}c1$	12	6.698	6.698	10.299	120	1.28, 1.29	142.91
"Q7"	$Fd\bar{3}m$	8	6.440	6.440	6.440	–	1.39	109.47
CuNCN:								
"N1"	$R\bar{3}m$	3	3.044	3.044	13.920	120	1.23	180.00
"N2"	$Pnma$	4	10.611	3.010	4.693	–	1.22, 1.23	174.16
"N3"	$I\bar{4}2d$	8	8.211	8.211	5.321	–	1.22, 1.23	174.99
"N4"	$Pbca$	8	9.639	5.519	6.214	–	1.22, 1.23	178.16
"N5"	$P2_1/c$	4	4.976	6.056	5.334	111.20	1.23	180.00
"N6"	$Pnma$	4	4.979	2.893	12.070	–	1.22, 1.23	177.09
"N7"	$I\bar{4}m2$	2	3.031	3.031	9.584	–	1.23	180.00
"N8"	Cm	2	4.024	4.063	5.109	108.49	1.18, 1.30	178.10
"N9"	$P2_1/c$	4	6.044	5.310	6.685	125.06	1.22, 1.23	171.33
"S1"	$P2_1/m$	2	5.004	5.590	3.511	87.73	1.22, 1.23	176.27
"S2"	$Cmcm$	4	3.039	9.574	5.176	–	1.20, 1.26	180.00
"S3"	$P6_3mc$	2	3.104	3.104	10.265	120	1.19, 1.27	180.00
"S4"	$Pbcm$	4	6.456	4.822	5.642	–	1.22, 1.23	179.59
"S5"	$Pnnm$	4	5.603	9.812	3.020	–	1.19, 1.26	174.92
"S6"	$Pnma$	4	5.283	5.960	5.234	–	1.22, 1.23	178.71
"S7"	$Pbca$	8	10.220	5.812	5.675	–	1.18, 1.28	177.54
"S8"	$C2/c$	8	9.291	5.586	12.071	149.74	1.20, 1.25	175.60
"S9"	$P2_1/c$	4	2.909	6.099	9.169	90.13	1.22, 1.23	178.90
"S10"	$R3m$	6	3.115	3.115	30.630	120	1.19, 1.28	180.00
"Q1"	$P6_3/mmc$	2	3.098	3.098	9.135	120	1.23	180.00
"Q2a"	$P4/nmm$	2	3.635	3.635	6.559	–	1.19, 1.28	180.00
"Q2b"	$P4/nmm$	2	3.919	3.919	5.778	–	1.23	180.00
"Q3a"	$Pnma$	4	5.065	3.197	9.483	–	1.20, 1.25	179.63
"Q3b"	$Pnma$	4	5.427	5.011	6.646	–	1.22, 1.23	176.06
"Q4"	$Pa\bar{3}$	4	5.250	5.250	5.250	–	1.23	180.00
"Q5"	$P6_3/mmc$	4	2.969	2.969	19.860	120	1.23	180.00
"Q6"	$P\bar{3}c1$	12	7.391	7.391	10.493	120	1.22, 1.24	178.18
"Q7"	$Fd\bar{3}m$	8	6.474	6.474	6.474	–	1.40	109.47

Fig. 3. Total energy *vs.* molar volume for the hypothetical binary *M*(NCN) structures considered (*M* = Mn, Fe, Co, Ni or Cu).

AgOCN) shows two rather different C-N bond lengths (1.20 Å and 1.27 Å); this structural type, with an asymmetrical N≡C-N^{2-} 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 NCN^{2-} 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. Ca^{2+} and Sr^{2+} cations are "hard" ions with large η values (19.5 eV and 16.3 eV, respectively [29]) and predominantly ionic bonding to the NCN^{2-} units; as a consequence, CaNCN and SrNCN are *carbodiimides* (see Fig. 1, left). On the contrary, Ag^{+}, Hg^{2+} and Pb^{2+} 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 NCN^{2-} unit; as a result, Ag$_2$NCN, 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
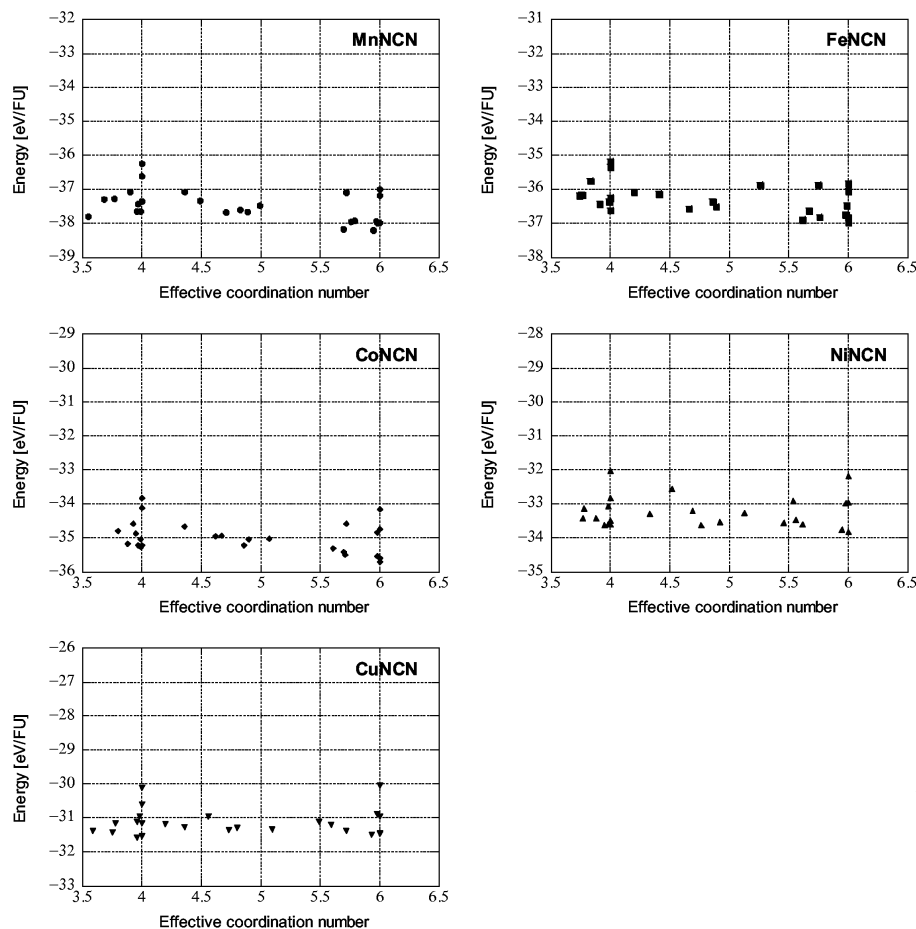
Fig. 4. Total energy *vs.* effective coordination number for the hypothetical quasi-binary *M*(NCN) structures considered (*M* = Mn, Fe, Co, Ni, Cu). A coordination number close to 6 is indicative of (slightly) lower energy values.

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.
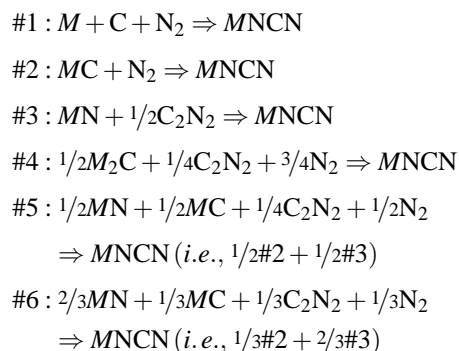
Thermochemistry

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 *M*N, *M*C and M_2C 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],

Table 5. Molar volumes [cm^3/mol] computed after geometry optimizations 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.

MnNCN	FeNCN	CoNCN	NiNCN	CuNCN
Q1– 20.34	**Q1– 19.42**	**Q1– 20.08**	**Q1– 20.87**	*N3– 27.05*
N2– 18.69	**N2– 18.75**	**N1– 19.96**	**N1– 20.58**	*N7– 26.51*
N1– 19.91	**N1– 19.38**	**N5– 19.90**	**N5– 20.77**	**N5– 22.56**
N5– 18.85	**Q3a– 19.69**	**S2– 20.00**	N6– 24.32	**N1– 22.42**
Q3a– 20.06	**S2– 19.48**	**Q3a– 20.05**	*Q3b– 25.82*	**Q1– 22.87**
Q5– 18.80	**N5– 19.05**	**N2– 19.41**	*N3– 25.33*	*S3– 25.79*
S2– 19.87	*N3– 22.84*	*N3– 24.00*	*S1– 26.94*	*S10– 25.83*
S10– 20.00	N4– 19.53	*S10– 22.62*	**S2– 20.94**	**N2– 22.57**
N4– 20.02	*S10– 21.19*	N6– 23.42	**N2– 21.60**	N6– 26.17
N6– 24.98	N6– 23.53	*N7– 23.30*	**S9– 23.78**	**S9– 24.49**
S1– 26.31	**Q5– 19.01**	*S3– 22.62*	N7– 24.36	N9– 26.44
Q3b– 22.71	Q3b– 22.44	S9– 24.14	**Q3a– 21.46**	**S8– 23.76**
S9– 25.52	*S1– 24.26*	*S1– 24.01*	S3– 23.53	N4– 24.88
S8– 21.76	S9– 24.61	**S8– 20.46**	*S10– 23.76*	**S2– 22.67**
N3– 23.30	N7– 22.20	S5– 21.25	S5– 22.41	**S4– 26.44**
N7– 31.16	S3– 26.52	N4– 20.89	**S8– 20.95**	S5– 25.00
N9– 25.56	S7– 22.66	*Q3b– 22.49*	N4– 22.92	*S7– 25.37*
S5– 23.34	**S8– 20.53**	**Q5– 19.98**	N9– 22.40	*S1– 29.55*
S7– 22.61	S5– 21.39	*S7– 23.95*	S7– 23.43	*S6– 24.81*
S3– 24.29	N8– 22.15	N9– 21.62	*S6– 24.18*	**Q3a– 23.12**
Q6– 19.83	N9– 23.71	**Q4– 19.45**	**Q5– 21.13**	N8– 23.85
S4– 22.59	**Q4– 18.61**	N8– 22.54	**Q4– 20.50**	**Q4– 21.78**
N8– 22.87	**S4– 21.48**	**S4– 20.82**	**S4– 21.86**	*Q3b– 27.21*
S6– 25.62	**Q6– 19.47**	*S6– 23.32*	*Q2b– 24.71*	**Q5– 22.82**
Q4– 18.99	*S6– 21.49*	**Q6– 19.43**	N8– 22.49	*Q2b– 26.72*
Q2b– 25.60	*Q2a– 23.55*	*Q2b– 23.51*	**Q6– 20.08**	*Q2a– 26.09*
Q2a– 24.16	*Q2b– 25.06*	*Q2a– 24.18*	*Q2a– 25.18*	**Q6– 24.91**
Q7– 20.96	Q7– 20.29	Q7– 20.01	Q7– 20.11	Q7– 20.43

VC ($Fm\bar{3}m$) [32], Fe$_2$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:

$$\#1 : M + C + N_2 \Rightarrow MNCN$$

$$\#2 : MC + N_2 \Rightarrow MNCN$$

$$\#3 : MN + \tfrac{1}{2}C_2N_2 \Rightarrow MNCN$$

$$\#4 : \tfrac{1}{2}M_2C + \tfrac{1}{4}C_2N_2 + \tfrac{3}{4}N_2 \Rightarrow MNCN$$

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

$$\#6 : \tfrac{2}{3}MN + \tfrac{1}{3}MC + \tfrac{1}{3}C_2N_2 + \tfrac{1}{3}N_2$$
$$\Rightarrow MNCN\,(i.e.,\ \tfrac{1}{3}\#2 + \tfrac{2}{3}\#3)$$

As introduced in the theoretical section, calculated reaction energies – expected to be very close to the actual reaction enthalpies ΔH_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_2N_2, N_2) as educts, having important implications for the Gibbs energies ΔG_R: If cyanamides/carbodiimides are to be sought for, *high-temperature routes should be avoided* at all costs because there is an *entropic destabilization* of cyanamide/carbodiimide 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 = Fe, Co or Ni), showing that obtaining cyanamides/carbodiimides starting from M_2C 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 MC 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(NCN) 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 ΔG_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/carbodiimide 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 instabilities is re-

Reaction	Educts for the synthesis of M(NCN)	MnNCN	FeNCN	CoNCN	NiNCN	CuNCN
#1	$M + C + N_2$	+044.8	+077.3	+101.5	+123.8	+144.8
#2	$MC + N_2$	−011.5	−030.5	−043.9	−086.4	−182.6
#3	$MN + 1/2C_2N_2$	−021.8	−019.8	−036.0	−089.4	−173.2
#4	$1/2M_2C + 1/4C_2N_2 + 3/4N_2$	−011.8	+005.0	+032.2	+031.7	−051.6
#5	$1/2MN + 1/2MC + 1/4C_2N_2 + 1/2N_2$	−016.6	−025.2	−040.0	−087.9	−177.9
#6	$2/3MN + 1/3MC + 1/3C_2N_2 + 1/3N_2$	−018.4	−023.4	−038.6	−088.4	−176.2

Table 6a. ΔE values [kJ/mol M(NCN)] computed for the synthesis of binary M(NCN) compounds from various educts on the basis of the GGA (Perdew-Wang 91).

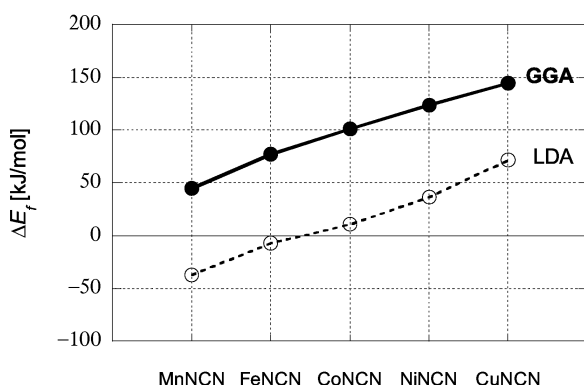| Reaction	Educts for the synthesis of M(NCN)	MnNCN	FeNCN	CoNCN	NiNCN	CuNCN
#1	$M + C + N_2$	−037.0	−007.1	+010.7	+036.5	+071.6
#2	$MC + N_2$	−083.0	−081.1	−119.2	−157.3	−252.6
#3	$MN + 1/2C_2N_2$	−064.2	−051.6	−093.4	−141.1	−218.3
#4	$1/2M_2C + 1/4C_2N_2 + 3/4N_2$	−099.3	−068.7	−057.8	−051.4	−133.9
#5	$1/2MN + 1/2MC + 1/4C_2N_2 + 1/2N_2$	−073.6	−066.4	−106.3	−149.2	−235.5
#6	$2/3MN + 1/3MC + 1/3C_2N_2 + 1/3N_2$	−070.5	−061.4	−102.0	−146.5	−229.8

Table 6b. Same as above but on the basis of the LDA.

Fig. 5. Evolution of the formation energy of binary M(NCN) compounds from the elements as a function of the transition metal M within the GGA approach; LDA results are given for comparison.

lated to the continuous filling of anti-bonding (t_{2g}) and strongly anti-bonding (e_g) d levels: thus, the higher the number of d electrons, the more destabilizing the effect. Recall that, within an octahedral coordination, the high-spin electronic configurations are $t_{2g}^3 e_g^2$, $t_{2g}^4 e_g^2$, $t_{2g}^5 e_g^2$, $t_{2g}^6 e_g^2$, and $t_{2g}^6 e_g^3$ for the Mn, Fe, Co, Ni and Cu phases.

The theoretical result that all M(NCN) compounds are enthalpically unstable comes as a surprise but immediately explains why no such phase has been reported so far. Without being too speculative, synthetic attempts have probably been carried out already, without success. On the other hand, the positive reaction (or formation) enthalpies (between *ca.* +45 and +145 kJ/mol if compared to the elemental states) need to be compared with likewise unstable materials which have been known for decades, *e.g.*, AgSCN ($\Delta H_f = +88$ kJ/mol), CuCN (+95 kJ/mol), Hg(SCN$_2$) (+201 kJ/mol) [24], and, without C-N bonds, Ni$_3$C (+68 kJ/mol), FeS (+102 kJ/mol), CuN$_3$ (+252 kJ/mol), Pb(N$_3$)$_2$ (+437 kJ/mol), and CoSO$_4$ (+888 kJ/mol) [24]; obviously, the positive formation enthalpies predicted for M(NCN) are not exceedingly high. Nonetheless, it is clear that the synthesis of M(NCN) will be unsuccessful if the elements are used as educts; therefore, alternative strategies need to be sought for. For example, a metathesis such as

$$MX_2 + A(NCN) \Rightarrow M(NCN) + AX_2$$
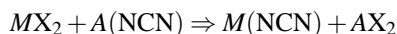
in which A(NCN) symbolizes a not exceedingly stable cyanamide/carbodiimide and AX_2 is an exceptionally stable halide – probably highly volatile such that it can be removed from the equilibrium – appears to be a reasonable starting point; low-temperature routes are nonetheless needed. Corresponding synthetic 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 prepared. 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 materials; nonetheless, their syntheses are proposed for the earlier 3d metals (Mn and Fe), not from the elements but through exchange reactions at relatively low temperatures.

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.

[1] M. G. Down, M. J. Haley, P. Hubberstey, R. J. Pulham, A. E. Thunder, J. Chem. Soc., Chem. Commun. 52 (1978).

[2] M. Becker, M. Jansen, Solid State Sci. **2**, 711 (2000).

[3] U. Berger, W. Schnick, J. Alloys Compd. **206**, 179 (1994).

[4] N. G. Vannerberg, Acta Chem. Scand. **16**, 2263 (1962).

[5] R. Riedel, A. Greiner, G. Miehe, W. Dressler, H. Fuess, J. Bill, F. Aldinger, Angew. Chem. Int. Ed. Engl. **36**, 603 (1997).

[6] R. Dronskowski, Z. Naturforsch. **50b**, 1245 (1995).

[7] X. Liu, A. Decker, D. Schmitz, R. Dronskowski, Z. Anorg. Allg. Chem. **626**, 103 (2000).

[8] M. Becker, M. Jansen, Z. Anorg. Allg. Chem. **626**, 1639 (2000).

[9] X. Liu, P. Müller, P. Kroll, R. Dronskowski, Inorg. Chem. **41**, 4259 (2002).

[10] X. Liu, R. Dronskowski, Z. Naturforsch. **57b**, 1108 (2002).

[11] G. Kresse, J. Hafner, J. Phys. Cond. Matt. **6**, 8245 (1994).

[12] G. Kresse, J. Hafner, Phys. Rev. B **49**, 14251 (1994).

[13] G. Kresse, J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).

[14] G. Kresse, J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

[15] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[16] G. Kresse, D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[17] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[18] P. E. Blöchl, O. Jepsen, O. K. Andersen, Phys. Rev. B **49**, 16223 (1994).

[19] H. J. Monkhorst, J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[20] H. Hellmann, Einführung in die Quantenchemie, Deuticke, Leipzig, Wien (1937).

[21] R. P. Feynman, Phys. Rev. **56**, 340 (1939).

[22] J. P. Perdew, in P. Ziesche, H. Eschrig (eds): Electronic Structure of Solids, Akademie Verlag, Berlin (1991).

[23] J. P. Perdew, K. Burke, Y. Wang, Phys. Rev. B **54**, 16533 (1996).

[24] R. Blachnik: Elemente, anorganische Verbindungen und Materialen, Minerale; J. D'Ans, E. Lax: Taschenbuch für Chemiker und Physiker; Springer-Verlag, Berlin, Heidelberg, New York (1998).

[25] G. A. Landrum, B. Eck, R. Dronskowski, Mater. Sci. Forum **325 – 326**, 105 (2000).

[26] P. Kroll, B. Eck, R. Dronskowski, Adv. Mater. **12**, 307 (2000).

[27] G. O. Brunner, D. Schwarzenbach, Z. Kristallogr. **133**, 127 (1971).

[28] X. Liu, P. Müller, P. Kroll, R. Dronskowski, W. Wilsmann, R. Conradt, ChemPhysChem **4**, 725 (2003).

[29] R. G. Pearson: Chemical Hardness, Wiley-VCH, Weinheim, New York (1997).

[30] K. Suzuki, H. Morita, T. Kaneko, H. Yoshida, H. Fujimori, J. Alloys Compd. **201**, 11 (1993).

[31] K. Suzuki, T. Kaneko, H. Yoshida, H. Morita, H. Fujimori, J. Alloys Compd. **224**, 232 (1995).

[32] J. Pflueger, J. Fink, W. Weber, K.-P. Bohnen, G. Crecelius, Phys. Rev. B **30**, 1155 (1984).

[33] Y. Hirotsu, S. Nagakura, Acta Metall. **20**, 645 (1972).

[34] J. Clarke, K. H. Jack, J. Phys. Soc. Jpn. **16**, 1213 (1961).

[35] M. Becker, M. Jansen, Acta Crystallogr. C **57**, 347 (2001).

[36] M. Becker, J. Nuss, M. Jansen, Z. Naturforsch. **55b**, 383 (2000).

[37] D. Britton, J. D. Dunitz, Acta Crystallogr. **18**, 424 (1965).

[38] J. C. Barrick, D. Canfield, B. C. Giessen, Acta Crystallogr. B **35**, 464 (1979).

[39] D. L. Smith, V. I. Saunders, Acta Crystallogr. B **38**, 907 (1982).

[40] C. Akers, S. W. Peterson, R. D. Willett, Acta Crystallogr. B **24**, 1125 (1968).

[41] D. L. Smith, J. E. Maskasky, L. R. Spaulding, J. Appl. Crystallogr. **15**, 488 (1982).

[42] M. A. Irving, M. M. Elcombe, T. F. Smith, Austral. J. Phys. **38**, 85 (1985).

[43] M. Kabesova, M. Dunaj-Jurco, M. Serator, J. Gazo, Inorg. Chim. Acta **17**, 161 (1976).

[44] I. Lindqvist, Acta Crystallogr. **10**, 29 (1957).

[45] D. D. Swank, R. D. Willett, Inorg. Chem. **4**, 499 (1965).

[46] D. L. Smith, V. I. Saunders, Acta Crystallogr. B **37**, 1087 (1981).

[47] D. B. McWhan, M. Marezio, J. P. Remeika, J. P. Dernier, Phys. Rev. B **5**, 2552 (1972).

[48] A. R. Lennie, S. A. T. Redfern, P. F. Schofield, D. J. Vaughan, Miner. Mag. **59**, 677 (1995).

[49] H. E. King Jr., C. T. Prewitt, Acta Crystallogr. B **38**, 1877 (1982).

[50] E. Nowack, D. Schwarzenbach, T. Hahn, Acta Crystallogr. B **47**, 650 (1991).

[51] Y. Takeuchi, Y. Kudoh, G. Sato, Z. Kristallogr. **173**, 119 (1985).

[52] V. van Laar, Phys. Rev. **156**, 654 (1967).

[53] P. Lightfoot, F. Krok, J. L. Nowinski, P. G. Bruce, J. Mater. Chem. **2**, 139 (1992).