

Octacoordinate Carbon Atom in Tetra(metalloamino)methanes CN_4M_4 ($M = Be, Mg, Ca$): Quantum-Chemical Investigation

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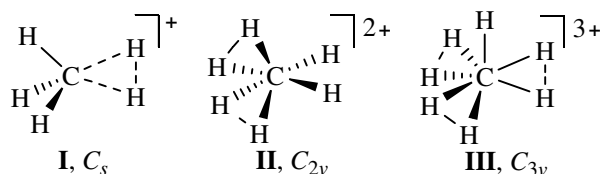
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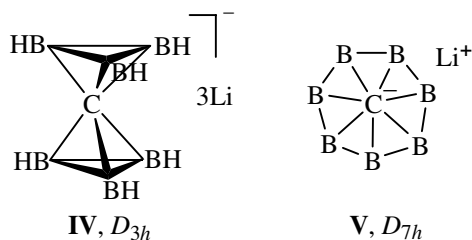
Abstract—Quantum-chemical methods, ab initio [MP2(full)/6-311+G**] and density functional theory (B3LYP/6-311+G**), were applied to investigation of the electronic and spatial structure of tetraaminomethane derivatives CN_4M_4 ($M = Be, Mg, Ca$) both in classic and nonclassic isomeric forms. For all compounds structurally stable nonclassic isomeric forms were found with an octacoordinate carbon atom. The CN_4Be_4 is energetically most stable in a classic structure with a tetracoordinate carbon atom, whereas CN_4Mg_4 and CN_4Ca_4 are more stable in nonclassic structures with an octacoordinate carbon center.

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Investigation of nonclassic systems with hypercoordinate atoms of main subgroups elements is of great interest for selection of new structural motifs in designing novel types of chemical compounds [1]. A special attention of researchers is attracted by the chemistry of hypercoordinated carbon that has started since the discovery of methonium cation CH_5^+ (**I**) [2] containing a pentacoordinate carbon center. Later systems were discovered with hexa- and heptacoordinate carbon atoms whose simplest representatives are di- (**II**) [3] and triprotonated (**III**) methane molecules [4].

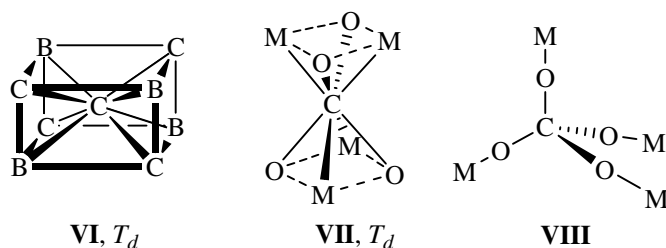


Nowadays quite a number of more complex organic, organoelemental, and organometallic systems has been



found containing hypercoordinate carbon; sandwich anion **IV** is an example of hexacoordination [5], and flat anion **V**, of heptacoordination [6].

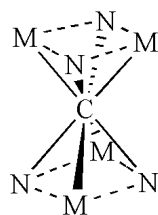
The hexa- and heptacoordination are not the limiting coordination types for the carbon atom. For instance, in carbide clusters of nickel $[CNi_8(CO)_{16}]^{2-}$ and cobalt $[CCo_8(CO)_{18}]^{2-}$ [7], and also in a polythium compound CLi_{12} [8] the carbon atom coordinates eight metal centers. Recently quantum-chemical calculations revealed an octacoordination of the endohedral carbon in organoboron cluster **VI** [9] and also in orthocarbonates **VII** [10]. The stabilization of orthocarbonic acid salts **VII** is based on the multicenter interaction of alkali metals with the oxoanion, and as a result the nonclassic octacoordinate structure **VII** proved to be energetically more favorable than the classic tetracoordinate form **VIII** [10].



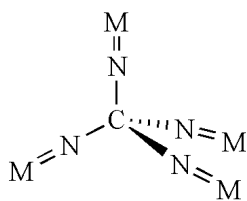
It is presunable that systems **IX**, isoelectronic to orthocarbonates **VII**, where the oxygen atoms are

replaced by nitrogen and the first group metals by the metals of the second group, would be also sufficiently stable with the central octacoordinate carbon atom.

The goal of this study was the investigation of structural and electronic characteristics of nonclassic compounds **IX** and of the possibility of their energy stabilization compared with the isomeric classic systems of **X** type.



IXa-IXc, T_d



Xa-Xc, T_d

Quantum-chemical calculations were carried out by the restricted Hartree-Fock method (RHF) taking into account the correlation of all (valence and core) electrons by the second order perturbation theory of Møller-Plesset [MP2(full)] [11] and by the method of density functional theory (DFT) [11] with triparametric potential B3LYP

in a valence-split basis 6-311+G** applying the software package GAUSSIAN-03 [12]. Identification of all stationary points was performed by Hesse matrix calculation. The topologic analysis of the total electron density distribution by Bader method (AIM-analysis) [13] was done with the use of original program package AIMPAC [14]. The graphical images of molecular structures presented in the figures were obtained by PD program (ORTEP mode) in the framework of the program package PC MODEL [15]. All calculations were performed in the gas phase approximation without accounting for the solvent effect.

Structure and stability of systems CN_4Be_4 .

According to the calculations done for the system CN_4Be_4 isomers **IXa** and **Xa** and also fenestrane structure **XIa** correspond to energy minima ($\lambda = 0$, here and hereinafter λ is the number of negative eigenvalues of the Hesse matrix in this point) on the potential energy surface (PES). The calculated structural and electronic characteristics of these forms are presented in Fig. 1, and energy data, in the table. The formation of nonclassic system **IXa** requires insignificant change in the C-N bond lengths in the range 0.001 (DFT) and 0.014 Å (MP2)

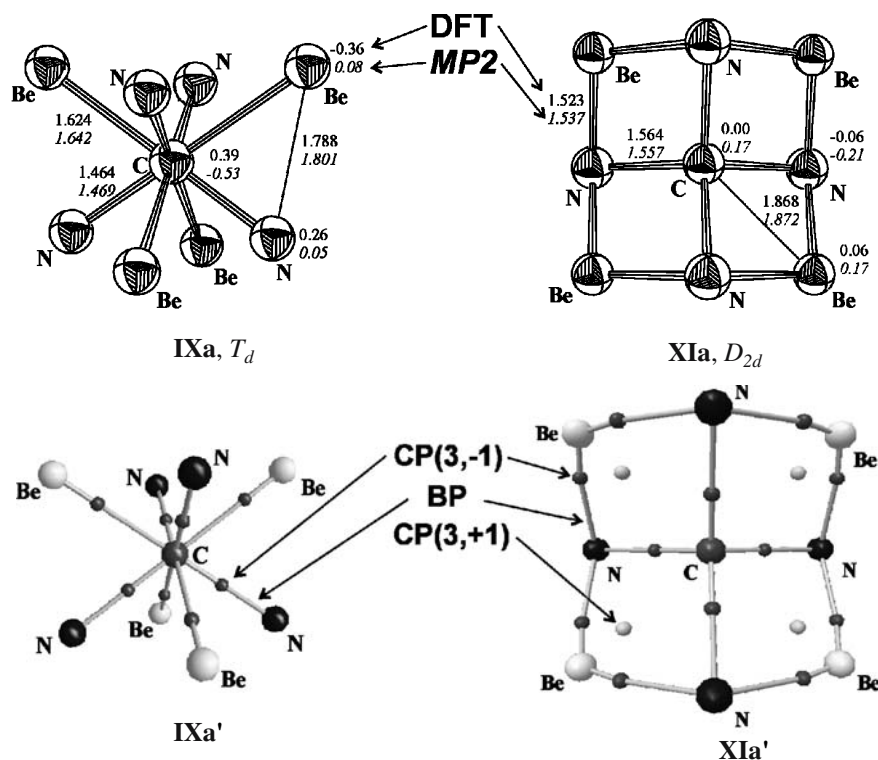


Fig. 1. Geometric characteristics and charges on atoms (according to Mulliken) for systems **IXa** and **XIa** calculated by methods DFT (B3LYP/6-311+G**) and ab initio [MP2(full)/6-311+G**]. Here and hereinafter the bond lengths are in Angstrom units. Bader's molecular graphs **IXa'-IXc'**, **XIa'-XIc'** of systems **IXa-IXc**, **XIa-XIc** are given in the bottom part of the figure; BP, Bader's bond path, CP (3, -1) is the critical point of the bond path, CP (3, +1) is the critical point of the ring.

Calculation results for structures **IXa–IXc**, **Xa**, and **XIa–XIc** by methods DFT (RB3LYP/6-311+G**) and MP2 [RMP2(full)/6-311+G**]

Structure	Method	E_{total}^a	λ^b	ZPE^c	$\omega_1/i\omega^d$	ΔE^e	ΔE_{ZPE}^f
IXa , T_d	DFT	–316.05943	00	0.03021	233	102.56	99.89
	MP2	–315.30277		0.03039	255	86.14	83.64
IXb , T_d	DFT	–1057.46306	00	0.02383	196	00	00
	MP2	–1055.63370		0.02327	194		
IXc , T_d	DFT	–2967.63244	00	0.02122	154	00	00
	MP2	–2964.96938		0.02055	153		
Xa , D_{2d} T_d	DFT	–315.78297	00	0.02846	17	276.05	272.282
	MP2	–315.01333		0.03047	126	267.76	65.32
XIa , D_{2d}	DFT	–316.22288	00	0.03447	271	00	00
	MP2	–315.44004		0.03437	267		
XIb , D_{2d}	DFT	–1057.41999	00	0.02191	25	27.02	25.82
	MP2	–1055.58630		0.02242	30	29.75	29.21
XIc , D_{2d}	DFT	–2967.52769	11	0.01990	<i>i</i> 56	65.73	64.90
	MP2	–2964.86138		0.02191	<i>i</i> 57	67.77	68.62

^a E_{total} , a.u. is total energy, 1 a.u. = 627.5095 kcal mol^{–1}.

^b λ is the number of negative Hessian eigenvalues.

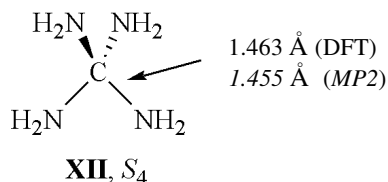
^c ZPE , a.u. is the energy of zero harmonic oscillations.

^d $\omega_1/i\omega$, cm^{–1} is the magnitude of the least or imaginary harmonic oscillation frequency.

^e ΔE , kcal mol^{–1} is the relative isomers energy.

^f ΔE_{ZPE} , kcal mol^{–1} is the relative isomers energy taking into account ZPE .

compared with tetraaminomethane (**XII**) whose calculated lengths of C–N bonds are given below.

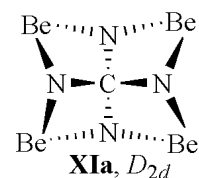


The calculated bond lengths C–Be in compound **IXa** is by ~0.03 Å shorter than the sum of covalent radii of C and Be atoms (1.66 Å [16]) indicating the large covalent contribution into this bond. The NBO-analysis [17] performed also suggested the covalent character of C–N and C–Be bonding in compound **IXa**. The C–Be bond in the system is stabilized mainly by donation of the electron density from the unshared electron pairs of nitrogen both to the vacant s -orbitals of Be and to antibonding orbitals of the C–N bonds. Therewith the electron density transfer from the CN_4 fragment to each berillium atom in system **IXa** amounts to 0.36 a.u. of charge (DFT data). Bader's topologic analysis (molecular graph **IXa'** in Fig. 1) reveals the presence of bond paths between the central carbon atom and N and Be atoms in

system **IXa**. The latter is the necessary and sufficient condition for the existence of a chemical bond [13]. Thus the results obtained show that in structure **IXa** the carbon atom is octacoordinate.

Isomeric classic system **Xa** CN_4Be_4 according to the calculations also corresponds to an energy minimum on PES ($\lambda = 0$), but this structure is considerably less energetically favorable than nonclassic isomer **IXa**: by 173.5 (DFT) and 181.6 (MP2) kcal mol^{–1}, accounting for the zero oscillations, by 172.4 and 181.7) kcal mol^{–1} respectively (see the table).

On the PES of CN_4Be_4 exists one more the deepest minimum ($\lambda = 0$) **XIa** corresponding to a classical structure of D_{2d} symmetry (Fig. 1, table) where the atoms of Be and C are located in the same plane, and the frame CN_4 remains in a tetrahedral configuration; therewith system **XIa** is energetically more favorable than **IXa** by 102.6 (DFT) and 86.1 (MP2)) kcal mol^{–1}.



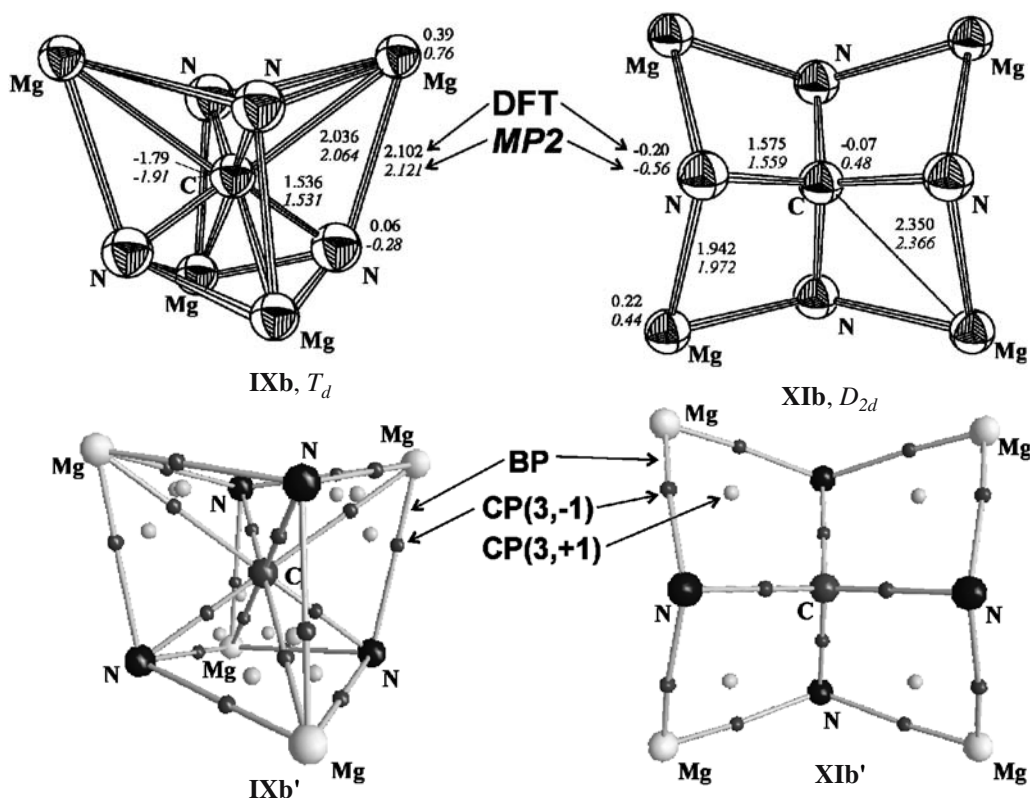


Fig. 2. Geometric characteristics and charges on atoms (according to Mulliken) for systems **IXb** and **XIb** calculated by methods DFT (B3LYP/6-311+G**) and ab initio [MP2(full)/6-311+G**].

The C–N bonds in structure **XIa** are by ~ 0.1 Å longer than in the tetraaminomethane (**XII**). The calculated interatomic distances C–Be in compound **XIa** exceed by ~ 0.2 Å the sum of covalent radii; the latter fact affects also the Bader's topologic analysis which indicates that Be atoms in system **XIa** are bicoordinate and are linked by valence bonds only to the nearest nitrogen atoms; the carbon atom also has its common tetracoordination (see molecular graph **XIa'** in Fig. 1).

Structure and stability of systems CN_4Mg_4 . In contrast to the berillium derivatives the most energetically feasible structure among isomeric systems CN_4Mg_4 is nonclassic structure **IXb** [energy minimum on PES ($\lambda = 0$)] and not the classic structure **XIb** with bicoordinate Mg atoms (Fig. 2, table). No isomer with classic structure **X** was found.

As show the calculations the C–N bonds in structure **IXb** are by ~ 0.07 Å longer than in the tetraaminomethane (**XII**). The C–Mg distance in compound **IXb** is by ~ 0.1 Å shorter than the sum of the covalent radii of C and Mg (2.13 Å [16]). The NBO-analysis performed showed that the C–Mg bond in compound **IXb** possesses pre-dominantly ionic character. The system is stabilized

mainly by donation of the electron density from the unshared electron pairs of nitrogen to the vacant *s*-orbitals of Mg. According to the topologic analysis the central carbon atom is linked not only to nitrogens but also to the magnesium atoms as show the bond paths between atoms C and N and Mg (see molecular graph **IXb'** in Fig. 2). Thus in structure **IXb** like in structure **IXa** the carbon atom is octacoordinate. The increased size of cation in going from berillium to magnesium also enhances the coordination opportunities of the metal and results in tetracoordinate magnesium and nitrogen atoms in system **IXb**, although the distances N–Mg are longer by ~ 0.05 Å than the sum of the corresponding covalent radii (2.06 Å [16]) (Fig. 2).

Classic system **XIb** CN_4Mg_4 of D_{2d} symmetry by ~ 30 kcal mol $^{-1}$ is less stable than **IXb** as calculated by both methods. The C–N bonds in compound **XIb** are longer by ~ 0.04 Å than in **IXb** and by ~ 0.11 Å longer than in tetraaminomethane (**XII**). Interatomic distances C–Mg exceed by more than ~ 0.2 Å the sum of covalent radii. According to the topologic analysis in system **XIb** like in compound **XIa** no bonds exist between the central carbon and Mg (see molecular graph **XIb'** in Fig. 2), and the carbon atom is tetracoordinate.

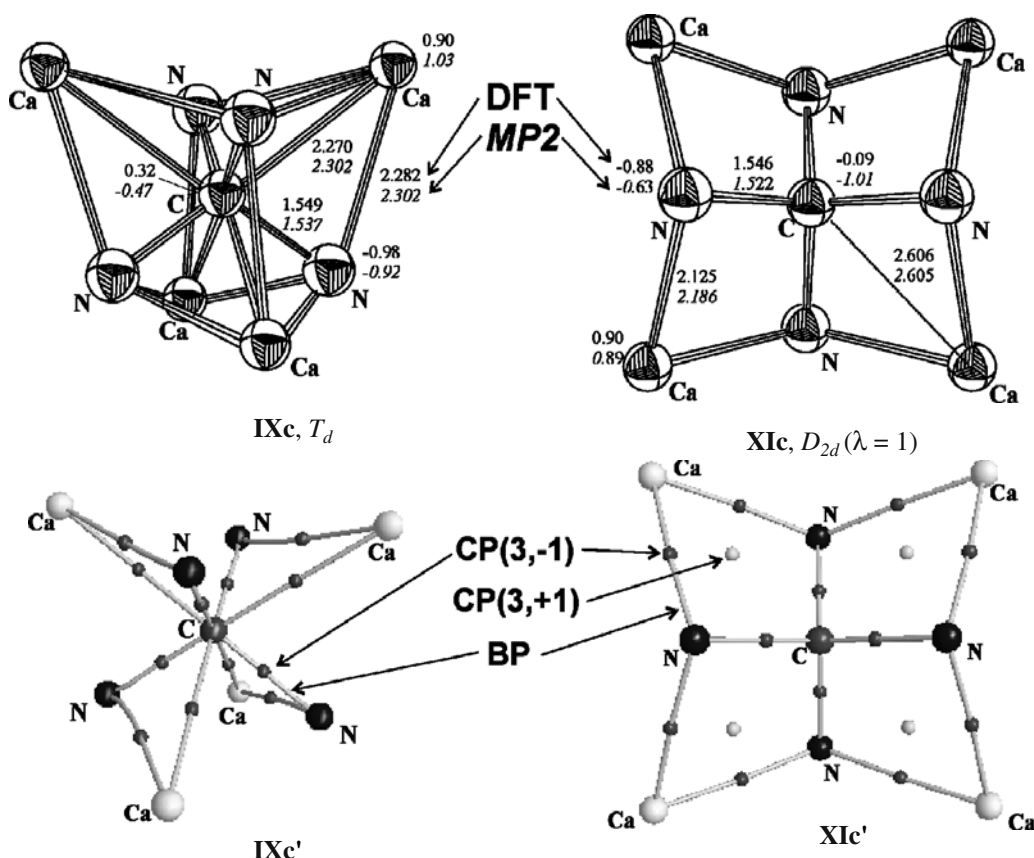


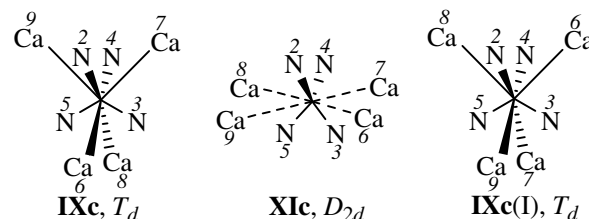
Fig. 3. Geometric characteristics and charges on atoms (according to Mulliken) for systems **IXc** and **XIc** calculated by methods DFT (B3LYP/6-311+G**) and ab initio [MP2(full)/6-311+G**].

Structure and stability of systems CN_4Ca_4 . Among CN_4Ca_4 isomers only the nonclassic system **IXc** corresponds to an energy minimum ($\lambda = 0$) on PES, whereas the classic isomer **XIc** according to the calculations corresponds to a transition state ($\lambda = 1$) (Fig. 3, table). Also no isomer **Xc** with a multiple N–Ca bond was found.

Of all structures **IX** the C–N bond is the most elongated in the Ca-derivative **IXc** (by ~ 0.13 Å) compared with tetraaminomethane (**XII**). The NBO-analysis performed showed that the bonding in compound **IXc** has ionic character. Like in compounds **IXa** and **IXb** the stabilization of compound **IXc** occurs mainly by donation of the electron density from the unshared electron pairs of nitrogen to the vacant s -orbitals of Ca, besides in system **IXc** a considerable donation of electron density is observed from the bonding orbitals of the C–N bonds to the vacant s -orbitals of Ca. The magnitude of the electron density transferred from the metal atoms to the CN_4 fragment in systems **IX** grows in the series Be, Mg, Ca in parallel with the decrease in electronegativity of these atoms (Figs. 1–3). As seen from Fig. 3, C–Ca distances in compound **IXc** are by ~ 0.2 Å shorter than

the sum of covalent radii of C and Ca (2.51 Å [16]) thus suggesting existence of C–Ca bonds in system **IXc**. The topologic analysis shows that like in compounds **IX** ($M = Be, Mg$) the carbon atom in structure **IXc** is bonded both to N and Ca atoms and therefore it is octacoordinate (see molecular graph **IXc'** in Fig. 3). It should be noted that unlike the analogous magnesium derivative **IXb** (Fig. 2) in system (**IXb**) the calcium cations and nitrogen atoms are bicoordinated and are linked in pairs with each other and with the central carbon atom (Fig. 3).

Isomeric structure **XIc** CN_4Ca_4 of D_{2d} symmetry unlike the corresponding Be- and Mg-derivatives **XIa** and **XIb** corresponds to a transition state ($\lambda = 1$) of a permutation rearrangement of diagonal *twist* type [18] (**IXc**) $\rightleftharpoons$ (**XIc**) $\rightleftharpoons$ [**IXc(I)**] consisting in migration of the Ca atoms around the tetrahedral fragment CN_4 .



The barrier to the rearrangement $(\mathbf{IXc}) \rightleftharpoons (\mathbf{XIc}) \rightleftharpoons [\mathbf{IXc(I)}]$ amounts respectively to 65.7 (DFT) and 67.8 (MP2) kcal mol⁻¹ without accounting for ZPE (see the table). The C–N bond lengths in compound **XIc** differ insignificantly from similar bonds in compound **IXc**. The distance C···Ca in compound **XIc** exceeds the sum of covalent radii by ~0.1 Å. According to the topologic analysis Ca atoms in system **XIc** like Be and Mg in compounds **XIa** and **XIb** are bicoordinated and have valence bonds only with the nearest nitrogen atoms, and the carbon possesses its common tetracoordination (see molecular graph **XIc'** in Fig. 3).

Thus in the same way as metals of the I group the metals of the II group can be used in simulation of new types of nonclassic systems. Structures **IX** CN₄M₄ (M = Be, Mg, Ca) considered in this study are a novel type of neutral stable nonclassic compounds with an octacoordinate carbon center. In the case of CN₄Be₄ classic system **XIa** is more energetically feasible containing a tetracoordinate carbon, and in compounds CN₄Mg₄ and CN₄Ca₄ nonclassic isomers prevail.

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