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Synthesis, Crystal Structure, and Properties of MnNCN, the First Carbodiimide of a Magnetic Transition Metal†

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Synthesis, single-crystal structure determination, and magnetic properties are reported for manganese carbodiimide, MnNCN. The presumably unstable but inert phase adopts the trigonal system ($R\bar{3}m$) with $a = 3.3583(4)$ Å, $c = 14.347(2)$ Å, $V = 140.13(3)$ Å^3, and $Z = 3$. Divalent manganese is octahedrally coordinated by nitrogen atoms at 2.26 Å, and the NCN^{2-} unit adopts the linear $[N{=}C{=}N]^{2-}$ carbodiimide shape with two C=N double bonds of 1.23 Å. MnNCN contains high-spin Mn(II) with five unpaired electrons and behaves like an antiferromagnet with an ordering temperature below 30 K.

Between 1927 and 1962, the early fertilizer CaNCN—*the* inorganic derivative of molecular cyanamide, H_2NCN—was structurally characterized,[1] yielding a distorted rock-salt type with an octahedral Ca^{2+} coordination. Since then, many other H_2NCN salts have been prepared, for example those containing alkaline (Li, Na)[2] or alkaline-earth metals (Mg, Ca, Sr, Ba),[3] main-group elements (In, Si, Pb),[4] late transition metals (Ag, Zn, Cd),[5] and also rare-earth metals (Eu, Ce).[6] In most cases (such as the archetype CaNCN, dubbed calcium *cyanamide* in the distant past), the NCN^{2-} anion exists in its so-called *carbodiimide* form, i.e., a linear $[N{=}C{=}N]^{2-}$ with two N=C double bonds, a finding easily rationalized by Pearson's HSAB concept.[7] While chemically hard cations (e.g., Ca^{2+}) favor ionic bonding to the symmetrical $[N{=}C{=}N]^{2-}$ anion, softer cations (e.g., Pb^{2+} or Ag^+) bind covalently to one side of the NCN^{2-} unit and induce the less symmetrical $[N{-}C{\equiv}N]^{2-}$ *cyanamide* shape. An interesting borderline case is given by the crystalline H_2NCN derivative of the soft Hg^{2+} ion because both a *metastable carbodiimide* polymorph—HgNCN(I), precipitated from strongly basic aqueous solution[8]—as well as a thermodynamically *stable cyanamide* polymorph, HgNCN(II), can be made, the latter by a stepwise H/Hg exchange under moderate pH conditions.[9]

In the realm of solid-state coordination chemistry, coordination polymers of the related but larger pseudohalide ligands dicyanamide $[N(CN)_2]^-$ and also tricyanomethanide $[C(CN)_3]^-$ have attracted considerable attention in recent years, partly due to the discovery of long-range magnetic ordering in some of those compounds.[10] Also, coordination polymers of the magnetic transition metals involving *small* pseudohalide ligands such as cyanide, azide, and thiocyanate have been studied for several decades. Our intention was to utilize the NCN^{2-} unit—a pseudo-sulfide anion by charge and spatial requirement—as a linker to communicate electronic information (e.g., magnetic exchange) between transition-metal centers.

Unfortunately, typical transition-metal M^{2+} cations prefer to form simple coordination complexes such as $[M(H_2NCN)_4]^{2+}$ involving the *neutral* cyanamide molecule only,[11] and it is difficult to remove the hydrogen atoms for making

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† Dedicated to Professor Peter Paetzold on the occasion of his 70th birthday and to Fudan University on the occasion of its centennial celebration.

(1) (a) Dehlinger, U. *Z. Kristallogr.* **1927**, *65*, 286. (b) Bredig, M. A. *J. Am. Chem. Soc.* **1942**, *64*, 1730. (c) Yamamoto, Y.; Kinoshita, K.; Tamaru, K.; Yamanaka, T. *Bull. Chem. Soc. Jpn.* **1958**, *31*, 501. (d) Vannerberg, N. G. *Acta Chem. Scand.* **1962**, *16*, 2263.

(2) (a) Down, M. G.; Haley, M. J.; Hubberstey, P.; Pulham, R. J.; Thunder, A. E. *J. Chem. Soc., Dalton Trans.* **1978**, 1407. (b) Harper, A.; Hubberstey, P. *J. Chem. Res. (S)* **1989**, *7*, 194. (c) Becker, M.; Nuss, J.; Jansen, M. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2505.

(3) (a) Berger, U.; Schnick, W. *J. Alloys Compd.* **1994**, *206*, 179. (b) Reckeweg, O.; DiSalvo, F. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 412. (c) Liao, W.; Dronskowski, R. *Acta Crystallogr. E* **2004**, *60*, 124.

(4) (a) Dronskowski, R. *Z. Naturforsch. B* **1995**, *50*, 1245. (b) Riedel, R.; Greiner, A.; Miehe, G.; Dressler, W.; Fuess, H.; Bill, J.; Aldinger, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 603. (c) Cooper, M. J. *Acta Crystallogr.* **1964**, *17*, 1452. (d) Liu, X.; Decker, A.; Schmitz, D.; Dronskowski, R. *Z. Anorg. Allg. Chem.* **2000**, *626*, 103.

(5) (a) Bowdem, F. P.; Montagu-Pollock, H. M. *Nature* **1961**, *191*, 556. (b) Becker, M.; Nuss, J.; Jansen, M. *Z. Naturforsch. B* **2000**, *55*, 383. (c) Becker, M.; Jansen, M. *Acta Crystallogr. C* **2001**, *57*, 347. (d) Baldinozzi, G.; Malinowska, B.; Rakib, M.; Durand, G. *J. Mater. Chem.* **2002**, *12*, 268.

(6) (a) Reckeweg, O.; DiSalvo, F. J. *Z. Anorg. Allg. Chem.* **2003**, *629*, 177. (b) Srinivasan, R.; Ströbele, M.; Meyer, H. J. *Inorg. Chem.* **2003**, *42*, 3406. (c) Liao, W.; Hu, C.; Kremer, R.; Dronskowski, R. *Inorg. Chem.* **2004**, *43*, 5884.

(7) Pearson, R. G. *Chemical Hardness*; Wiley-VCH: Weinheim, New York, 1997.

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

(9) (a) Liu, X.; Müller, P.; Kroll, P.; Dronskowski, R. *Inorg. Chem.* **2002**, *41*, 4259. (b) Liu, X.; Müller, P.; Kroll, P.; Dronskowski, R.; Wilsmann, W.; Conradt, R. *ChemPhysChem* **2003**, *4*, 725.

(10) (a) Batten, S. R.; Jensen, P.; Moubaraki, B.; Murray, K. S.; Robson, R. *Chem. Commun.* **1998**, 439. (b) Batten, S. R.; Murray, K. S. *Coord. Chem. Rev.* **2003**, *246*, 103. (c) Kutasi, A. M.; Harris, A. R.; Batten, S. R.; Moubaraki, B.; Murray, K. S. *Cryst. Growth Design* **2004**, *4*, 605.

(11) (a) Liu, X.; Kroll, P.; Dronskowski, R. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1682. (b) Liu, X.; Dronskowski, R. *Z. Kristallogr. NCS* **2002**, *217*, 118.

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MNCN phases. In addition, conventional high-temperature routes targeted at MNCN compounds have also turned out unsuccessful because they lead to the bare metals, amorphous carbon, and gaseous nitrogen. These disencouraging results and the nonexistence of these compounds find their explanation in quantum-chemical structure predictions of MNCN materials (M = Mn, Fe, Co, Ni, Cu) from density-functional theory (GGA)[12] which render *all* quasi-binary compounds as *unstable* in terms of both formation enthalpy ΔH_f and Gibbs formation energy ΔG_f. Thus, MNCN phases can only be made if accompanied by highly stable side-products or if the chemical equilibrium leading to MNCN is directed upon synthesis. For M = Mn, an octahedral coordination of the high-spin Mn^{2+} cation is also predicted.[12] Here, we report the successful synthesis of MnNCN using a metathesis route involving zinc carbodiimide and manganese(II) chloride as starting materials. The synthetic idea is motivated by the low melting temperature (260 °C) and also sublimation temperature (500 °C) of the product $ZnCl_2$ because the latter can be removed from the equilibrium directly upon formation, thereby enforcing MnNCN formation. Eventually, a green phase, MnNCN, is obtained upon carefully controlling the temperature, and single-crystals for X-ray structure determination result from crystal growth within a melt of lithium bromide.[13]

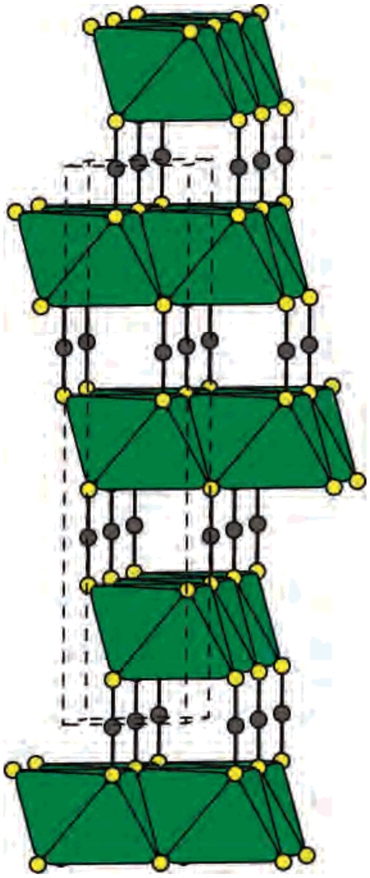

Figure 1. View of the crystal structure of MnNCN with MnN_6 octahedra (broken lines: unit cell).

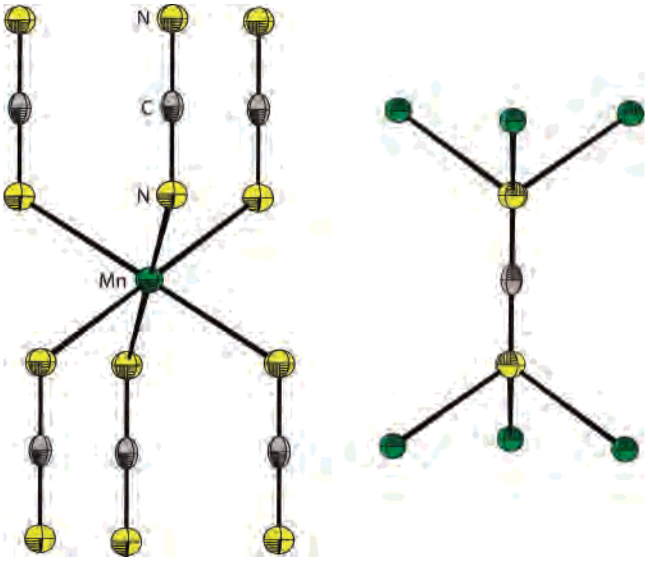

Figure 2. ORTEP drawing of MnNCN with thermal ellipsoids at the 90% probability level. Selected bond lengths (Å) and angles (deg): Mn−Mn = 3.358(4), N−Mn = 2.262(2), C−N = 1.227(4), N−Mn−N = 180, N−Mn−N = 95.9(1), N−Mn−N = 84.1(1), N−C−N = 180, C−N−Mn = 120.98(9), Mn−N−Mn = 95.9(1).

The crystal structure of manganese carbodiimide is isotypical with the one of CaNCN (and also the high-temperature phases of NaN_3, MgNCN, CdNCN, and *β*-SrNCN),[14] depicted in Figure 1. There are alternating layers of Mn^{2+} cations and NCN^{2-} anions along the trigonal axis, and the strictly linear anions (by reasons of space-group symmetry) are oriented perpendicular to the layers. Each divalent Mn is coordinated by six nitrogen atoms at Mn−N = 2.262(2) Å, in accord with predictions based on effective ionic radii (2.29 Å)[15] and bond-valence calculations (2.28 Å).[16] The resulting octahedron around Mn^{2+} (see Figure 2) is slightly squeezed with N−Mn−N = 95.9(1) and 84.1(1)°. The shortest $Mn^{2+}-Mn^{2+}$ distance, 3.358(4) Å, is identical with the *a* lattice parameter. Each nitrogen atom coordinates to three Mn(II) atoms and also binds to the carbon atom (coinciding with the inversion center) with C−N =1.227(4) Å; thus, the NCN^{2-} unit of MnNCN reflects perfect $D_{\infty h}$ (carbodiimide) symmetry based on the single-

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(12) Launay, M.; Dronskowski, R. *Z. Naturforsch. B* **2005**, *60*, 437.

(13) Synthesis: 0.211 g of ZnNCN and 0.279 g of $MnCl_2$ (1:1.2 molar ratio) were mixed under argon atmosphere, sealed in a quartz ampule, and heated to 600 °C for 3 days. The green MnNCN compound is rather inert in air and can be washed using ordinary water. Suitable crystals for single-crystal diffraction were obtained by the same reaction but using 2.0 g of LiBr as a solvent at 650 °C. According to atomic absorption spectroscopy, crystalline samples still exhibit very small Zn contaminations (with Zn presumably replacing Mn), and this is in accord with precise magnetic measurements (see text). The product is entirely free of Li and Br. The powder X-ray diffraction diagram is single-phase, and all reflections perfectly coincide with the single-crystal result.

(14) Crystallographic data for MnNCN: Formula weight = 94.962 g/mol, green hexagonal prisms (0.1 × 0.1 × 0.05 mm^3), trigonal $R\bar{3}m$, a = 3.3583(4) Å, c = 14.347(2) Å, V = 140.13(3) $Å^3$, Z = 3, T = 298(2) K, 610 reflections measured of which 68 were independent, Bruker SMART-APEX CCD diffractometer with Mo Kα radiation and θ_{max} = 30.36°. The structure was solved by the Patterson method, refined by full-matrix least-squares procedures based on F^2 (8 parameters) and converged to R_1 = 0.025 and wR_2 = 0.059 using anisotropic displacement parameters for all atoms; Mn on 3*a*, C on 3*b*, N on 6*c* with z = 0.5855(3). Additional structural details may be obtained from FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-415019.

(15) Shannon, R. D. *Acta Crystallogr. A* **1976**, *32*, 751.

(16) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr. B* **1991**, *47*, 192.

crystal X-ray data, just like the isotypical carbodiimide CaNCN.[17] This crystallographic and crystal−chemical finding is further corroborated by the infrared spectrum of MnNCN measured in KBr, exhibiting only a strong carbodiimide-typical asymmetrical vibration, ν_{as}(NCN) = 2049 cm^{-1}, plus another strong deformation vibration, δ(NCN) = 650 cm^{-1}. In contrast, the symmetrical ν_s signal (around 1200 cm^{-1}) is totally missing because such a breathing mode is IR-forbidden for the symmetrical $N{=}C{=}N^{2-}$ unit although it would be allowed for a cyanamide.[18] We emphasize that the here-found (and also predicted)[12] *carbodiimide* shape of MnNCN possibly indicates the first violation of the NCN^{2-} shape rule based on Pearson hardnesses η because the relatively soft Mn^{2+} (9.0 eV) resembles Pb^{2+} (8.5 eV) and points toward the cyanamide. Whether this behavior goes back to the consequences of spin polarization (see magnetic behavior below), we cannot say with certainty at the moment.

The magnetic behavior of MnNCN has been determined by SQUID magnetometry (MPMS-5S, Quantum Design, San Diego, CA) in the temperature range between 4 and 300 K and at applied fields B_0 between 0.5 and 5 T. The data were corrected for diamagnetic contributions using an increment of -44×10^{-11} m^{3}mol^{-1} (SI) where the value for NCN^{2-} has been taken from OCN^- (-26×10^{-11} m^{3}mol^{-1}) as a plausible replacement for the isoelectronic carbodiimide unit.[19] Figure 3 displays the results of the susceptibility measurements at $B_0 = 0.5$ T by means of a χ_m^{-1} vs. T plot where χ_m refers to the formula unit MnNCN. The insert shows the χ_m vs. T data below 100 K.

For temperatures above 150 K, Curie−Weiss behavior $\chi_m = C/(T - \theta)$ is observed with $C = 5.367 \times 10^{-5}$ m^{3}Kmol^{-1} and $\theta = -302$ K. Compared with an ideal 3d^5 high-spin system (Mn^{2+}, $S = {}^5/_2$, $C = 5.500 \times 10^{-5}$ m^{3}Kmol^{-1}, $\mu = 5.92\ \mu_B$),[20] the experimental C reflects five unpaired electrons ($\mu = 5.84\ \mu_B$) but is reduced by ca. 2.4% in accord with a small diamagnetic impurity due to Zn^{2+}. The negative θ value and the maximum of the molar susceptibility at 28 K are in favor of predominantly *antiferromagnetic* exchange interactions between the manganese centers. Susceptibility measurements at various applied fields do not show any field dependence for $T > 30$ K. At 25 K, however, a characteristic dependence of χ_m on the applied field strength is observed indicating the onset of a magnetic ordering. The high-spin behavior of Mn^{2+} and the antiferromagnetic coupling had been predicted before by first-principles electronic-structure theory.[12]

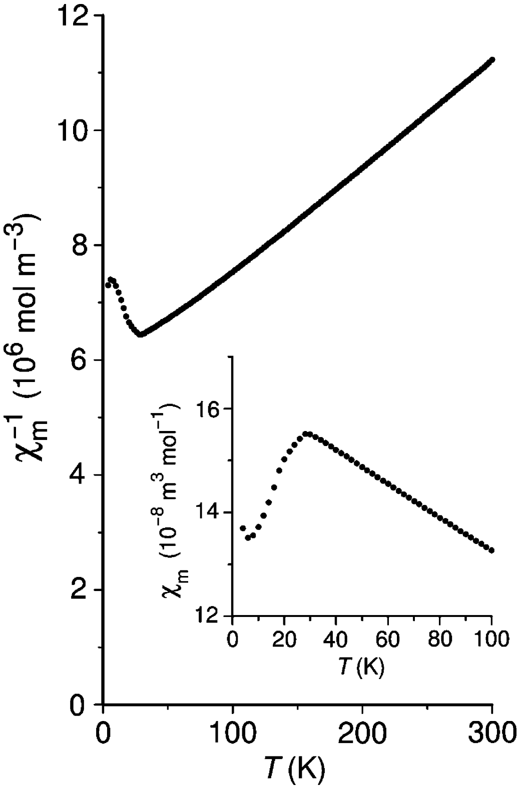

Figure 3. Magnetic susceptibility measurement of MnNCN given as χ_m^{-1} vs. T with the low-temperature region as a χ_m vs. T insert.

To explain the details of the antiferromagnetic mechanism, superexchange pathways Mn···N···Mn (end-on coordination mode) and Mn···N=C=N···Mn (end-to-end mode) have to be taken into consideration; see Figure 2. While the role of the azido bridge NNN^- in superexchange has been examined to some degree,[21] corresponding information is unavailable for the NCN^{2-} bridge at the moment. Neutron diffraction measurements targeted at the spin arrangements and the exchange mechanism (role of the carbodiimide unit) are under way.

Summarizing, we have achieved the synthesis and structural characterization of the first magnetic transition-metal carbodiimide phase, MnNCN. The compound, originally proposed as a thermodynamically unstable phase, is accessible by a metathesis reaction which may be extended to other transition metals and thus opens the path towards a whole series of related quasi-binary or quasi-ternary compounds.

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Supporting Information Available: Crystallographic files in CIF format for MnNCN. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The minute elongation of the central C atom (see Figure 2) is due to a regular atomic vibration but not a split position below and above the 3*b* site, in full accord with the infrared data. The corresponding (but less stable) split refinement results in a *z* coordinate of 0.495(8) instead of the correct $^1/_2$ and is characterized by significantly worse residual values.

(18) Reckeweg, O.; Simon, A. *Z. Naturforsch. B* **2003**, *58*, 1097.

(19) Weiss, A.; Witte, H. *Magnetochemie*; Verlag Chemie: Weinheim, Germany, 1973.

(20) Lueken, H. *Magnetochemie*; Teubner: Stuttgart, 1999.

(21) Miller, J. S., Drillon, M., Eds. *Magnetism: Molecules to Materials II*; Wiley-VCH: Weinheim, New York, 2001; ch. 9.