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FeNCN and $Fe(NCNH)_2$: Synthesis, Structure, and Magnetic Properties of a Nitrogen-Based Pseudo-oxide and -hydroxide of Divalent Iron

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The successful rational design of novel magnetic materials crucially depends on the combination of the right paramagnetic transition- or rare-earth metals together with diamagnetic polynuclear bridging ligands in order to ensure strong and directed magnetic "communication" between the adjacent centers in multiple dimensions. An ideal building block should easily form covalent bridges between the metal centers, and the bridging ligands themselves should be compact and also capable of mediating significant spin density. The cyanometalates, for example, have been known for many decades to serve as excellent starting materials for the synthesis of inorganic polymers with new magnetic properties.[1,2] Also, the azide anion (N_3^-) is another commonly used pseudohalide bridging ligand needed for the design of polynuclear transition-metal complexes with tuneable physical properties.[2]

For a couple of years, our own group has been concerned with another fascinating family of building blocks that stem from the cyanamide molecule H_2NCN. Its two anions, $HNCN^-$ and NCN^{2-}, have been used successfully by others and ourselves to prepare a large number of new solid-state materials comprising alkali metals,[3] alkaline-earth metals,[4] main-group elements,[5] d^{10} transition metals,[6] and also rare-earth metals,[7] albeit through largely differing synthetic routes. The doubly charged NCN^{2-} anion seems especially attractive to us because it stands for a pseudo-chalcogenide or even pseudo-oxide, thereby opening the path for an entirely new class of materials.

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In combination with 3d transition-metal cations, simple inorganic compounds such as the above-mentioned pseudo-oxides are especially attractive as candidates for magnetic materials. Despite having been predicted as being thermodynamically unstable on the basis of density-functional calculations,[8] we have explored several such solid-state (monohydro)cyanamide and carbodiimide compounds of the divalent 3d transition metals with d^5–d^9 electronic configurations.[9–13] In particular, the phases designated as MnNCN, CoNCN, NiNCN and CuNCN—the nitrogen-based analogues of the correlated oxides MnO, CoO, NiO, and CuO, which form the playing ground of modern solid-state physics—stand for a novel class of magnetic materials. In this communication, we report about the synthesis, structures, and magnetic properties of the two remaining monohydrocyanamide and carbodiimide representatives, namely $Fe(NCNH)_2$ (**1**) and FeNCN (**2**).

The reaction of $[Fe(NH_3)_6]^{2+}$ with cyanamide in aqueous solution under strict Schlenk-technique conditions yields $Fe(NCNH)_2$ (**1**), as a pale green precipitate upon removal of excess ammonia, and **1** turns out to be extremely air-sensitive. FeNCN (**2**) was made by carefully decomposing **1** in a halide salt flux at temperatures between 390 and 410 °C, and **2** crystallizes as dark-red platelets, which glitter a great deal; melamine is received as a by-product.

Alternatively, **2** can also be synthesized by the reaction of $FeCl_2$ with Li_2NCN although the limited purity of Li_2NCN poses further problems.[7d] Fortunately, **2** can be exposed to air for a couple of weeks without significant oxidative decay. X-ray powder diffraction (XRPD) was utilized to show that both materials are crystallographically phase-pure, and the new compounds are isomorphous with $M(NCNH)_2$ and MNCN (M = Co, Ni).[12,13] Owing to the excellent crystallinity of **1**, its structure refinement could be based on the well-resolved XRPD data shown in Figure 1, whereas, for the case of **2**, the presence of tiny crystals even allowed the collection and refinement of single-crystal data.

The orthorhombic crystal structure of iron (bis)monohydrocyanamide **1** is presented in Figure 2. The divalent iron

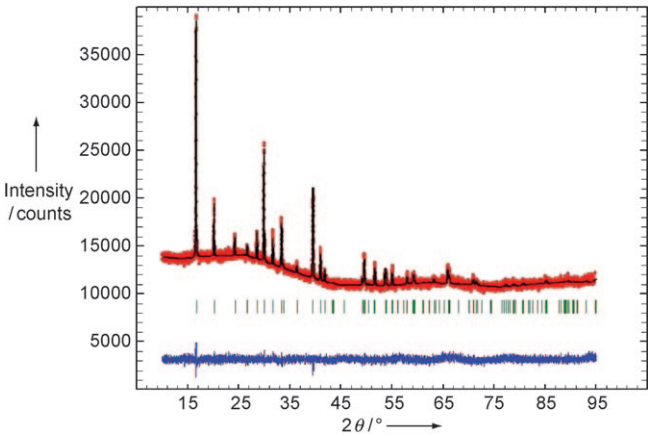

Figure 1. Rietveld refinement of the powder X-ray diffraction data of **1** on the basis of $Cu_{K\alpha 1}$ radiation, with the positions of the Bragg reflections given in green and the difference signal in blue.

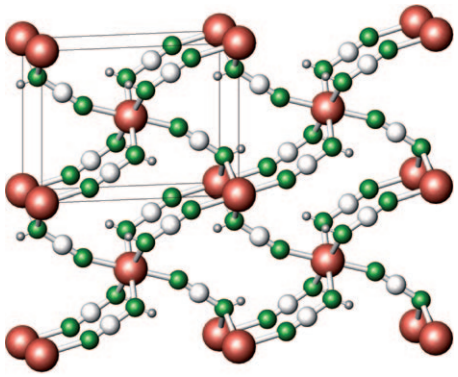

Figure 2. The crystal structure of **1** along the *c* axis. Color code: Fe: red; C: white; N: green; H: gray.

atoms alone adopt a body-centered orthorhombic Bravais lattice, although the space group is *Pnnm*. Each Fe^{2+} ion is coordinated by six nitrogen atoms, and the Fe–N distances arrive at $4\times2.220(5)$ Å and $2\times2.139(8)$ Å, such that the six Fe–N distances are very similar, although four of the N atoms are of amino and two are of nitrile type. The slightly flattened N_6 octahedra around Fe^{2+} are linked with each other by sharing edges along the short *c* axis, identical with the shortest Fe···Fe distance (3.3302(1) Å). Clearly, the overall packing bears a strong resemblance with the rutile type.

The cyanamide core of the $HNCN^-$ unit is practically linear with 173.7(12)°, and the monohydrocyanamide anions are arranged diagonally within the *ab* plane. The single H atom is bonded to the amino nitrogen atom and points into an empty void of the crystal structure. In addition, the XRPD resolution is sufficient to clearly confirm different C–N bond lengths (1.12(1) Å, single bond, and 1.35(1) Å, triple bond) indicative of the cyanamide character, in perfect coincidence with the data of the infrared spectra (see the Supporting Information, Figure S1), which exclude a carbodiimide structure by showing a strong symmetrical band $\nu_s(HN–C\equiv N) = 1198\ cm^{-1}$ which would not be allowed otherwise.

The hexagonal crystal structure of iron carbodiimide **2** may *formally* be considered a layered structure in which each "layer" consists of alternating M^{2+} and NCN^{2-} ions along *c*, as depicted in Figure 3. Within the *ab* plane, the

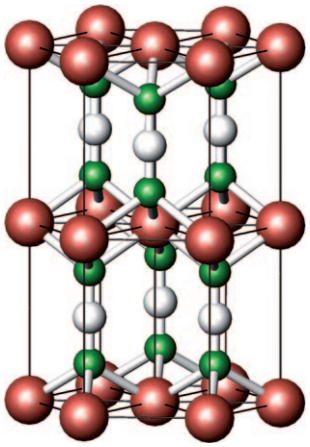

Figure 3. The crystal structure of **2** resembling the NiAs or 2H-stacking type of the delafossite structure type. Color code: Fe: red; C: white; N: green; H: gray.

Fe···Fe distance is 3.2689(2) Å. Each Fe^{2+} ion is coordinated by six nitrogen atoms leading to a slightly flattened N_6 octahedron with Fe–N = 2.201(6) Å. Given the symmetry of the unit cell, the NCN^{2-} units run parallel with the *c* axis, and the anions are strictly linear (N-C-N = 180°). Because of the octahedral coordination of Fe^{2+} and the trigonal-prismatic one of the NCN^{2-} unit as a consequence of space group $P6_3/mmc$, the crystal structure resembles the NiAs type or the 2H stacking variant of the delafossite ($Cu^{I}Fe^{III}O_2 \equiv$ Fe-[OCuO]) type.[14] The C=N double-bond length arrives at the expected 1.217(11) Å, and the anionic shape conforms to ideal $D_{\infty h}$ (carbodiimide) symmetry; for comparison, the C=N double-bonds in MnNCN, CoNCN and NiNCN are 1.227(4), 1.226(2) and 1.233(16) Å.[11,13] Consequently, the infrared spectrum of **2** (see Supporting Information, Figure S2) exhibits only a strong carbodiimide-type asymmetrical vibration, $\nu_{as}(NCN) = 2127\ cm^{-1}$, plus a strong deformation vibration, $\delta(NCN) = 645\ cm^{-1}$. In contrast, no symmetrical ν_s band (around $1200\ cm^{-1}$) is observed because such a breathing mode is IR-forbidden for the $[N=C=N]^{2-}$ carbodiimide unit, although it would be allowed for the less symmetrical cyanamide $[N–C\equiv N]^{2-}$ ion.

Within the crystal structures of **1** and **2**, it is clear that both Fe-N-Fe and Fe-NCN-Fe bridges will promote the formation of a magnetic coupling between adjacent spin centers. For comparison, it has been widely stated that the exchange type for the azide anion is, with only a few exceptions, generally ferromagnetic in nature for the end-on (EO) mode and antiferromagnetic for the end-to-end (EE) mode.[2] In the case of the monohydrocyanamide and carbo-

diimide ions, corresponding investigations are still in their infancy, and the present situation is furthermore complicated by the fact that in **1**, $HNCN^-$ is noncentrosymmetric and totally bonds to four atoms because one amino N atom connects to two Fe atoms and one H atom while a nitrile N atom bonds to only one Fe atom. In **2**, NCN^{2-} is centrosymmetric and bonds to three Fe atoms on each side. Nonetheless, **1** and **2** are composed of almost perfectly octahedral FeN_6 coordination environments with similar Fe–N distances around 2.2 Å. Note that the "layer-connected" FeN_6 octahedra in **2** are dimensionally reduced to "chain-connected" FeN_6 octahedra in **1** by the insertion of an extra EE-coordinating $HNCN^-$ anion. The first full elucidation of a corresponding carbodiimide magnetic structure is given by the very recent example of CuNCN, which turned out, through a combination of physical measurements and correlated first-principles calculations, to be a two-dimensional frustrated Heisenberg quantum antiferromagnet.[15]

The magnetic susceptibilities of the ground powder of **2** were determined by SQUID magnetometry (MPMS-5S, Quantum Design, San Diego) in the temperature range between 2 and 375 K at applied fields $0.05 \le B_0 \le 5$ T. The data were corrected for diamagnetic contributions using an increment of -42×10^{-11} $m^3 mol^{-1}$. The results of the susceptibility measurements by means of a χ_m versus T plot can be found in Figure 4.

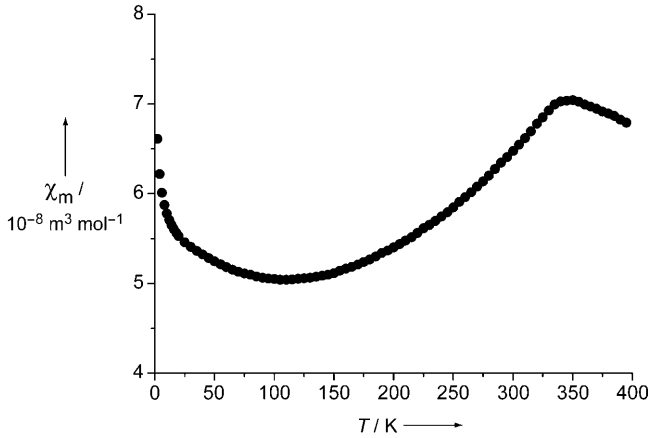

Figure 4. The molar magnetic susceptibility χ_m of iron carbodiimide **2** as a function of the temperature at an applied field of $B_0 = 0.1$ T.

The χ_m versus T plot of iron carbodiimide **2** exhibits a susceptibility maximum at $T(\chi_m{}^{max}) = 345$ K which we attribute to the Néel temperature T_N of FeNCN. Below 345 K the curve features a trend typical for an antiferromagnet. The signal increase at the low-temperature region may be caused by traces of a Curie-paramagnetic impurity. The χ_m data at $T > 345$ K correspond to $\mu_{eff} \approx 3.9$ (with $\mu_{eff} = 797.74\ [\chi_m T]^{1/2}$). This value is considerably lower than the 5.0–5.5 expected for mononuclear complexes of Fe^{II} with a $3d^6$ high-spin configuration in a regular octahedral surrounding by ligands of moderate strength, for example, NH_3 ($\Delta_{oct} \approx 12000\ cm^{-1}$).[16,17] The observed reduction of μ_{eff} below the spin-only value $\mu_{s.o.} = 4.9$ ($S = 2$) is obviously caused by antiferromagnetic spin–spin coupling mediated by superexchange, through the carbodiimide group, as well as by orbital quenching on account of the metal's distorted coordination polyhedron. Comparing $T_N = 175$ K of FeO[19] with $T(\chi_m{}^{max})$ of **2**, the antiferromagnetic interactions are significantly stronger in the carbodiimide.

With regard to the magnetic characterization of **1** (see Supporting Information, Figures S3–S5), the measured susceptibility data at $T \ge 250$ K are independent of the applied field, and they correspond to an effective magnetic moment μ_{eff} around 4.5. Just like for **2**, μ_{eff} is distinctly smaller than the spin-only value, caused by an antiferromagnetic spin-spin coupling. For $T < 250$ K, the molar susceptibility of **1** becomes field-dependent (see the corresponding hysteresis loops in the Supporting Information, Figure S4). At present the origin of the field dependence is unknown. It may be caused by a small amount of a paramagnetic/magnetically ordered impurity. Moreover, it is worth mentioning that weak ferromagnetism (spin canting) of **1** cannot be ruled out—note that the site symmetry of the iron atom in position 2*a* is 2/*m* or C_{2h}.

Given the existence of the presently known MNCN carbodiimide series (with M = Mn, Fe, Co, Ni, and Cu), a first comparison yields similarities and dissimilarities with oxides and chalcogenides. All MNCN phases contain octahedrally coordinated M^{2+} ions, and the crystal packing leads to molar volumes between 28.1 $cm^3 mol^{-1}$ (MnNCN) and 24.0 $cm^3 mol^{-1}$ (NiNCN) which results in a surprisingly constant volume increment of 22.6(5) $cm^3 mol^{-1}$ for the NCN^{2-} unit, extremely close to the S^{2-} anion (23 $cm^3 mol^{-1}$).[22] The occurrence of the [NiAs] and non-occurrence of the [NaCl] motif for FeNCN, CoNCN, and NiNCN also alludes to sulfide structural chemistry. Nonetheless, other, more "electronic", physical properties (such as magnetism, see above) and also the optical appearance clearly remind us of pseudo-oxides: MnNCN is green, FeNCN dark red, CoNCN orange-brown, NiNCN light-brown, and CuNCN black, quite close to the MO compounds. To shed more light on this interesting phenomenon, one might first want to quantitatively answer why MnNCN crystallizes in space group $R\bar{3}m$, whereas FeNCN adopts $P6_3/mmc$.

Summarizing, we have synthesized and structurally characterized the nitrogen-based analogues of iron(II) hydroxide and iron(II) oxide, namely $Fe(NCNH)_2$ (**1**) and FeNCN (**2**). Despite showing different $NCNH^-$ and NCN^{2-} bridging modes between the iron centers and, therefore, different topological packings, antiferromagnetic exchange couplings predominate in both solid-state structures. At the moment, (spin-polarized) neutron diffraction measurements together with first-principles GGA + *U* calculations are under way.

Experimental Section

To avoid the oxidation of Fe^{2+}, all experiments were carried out in a dry argon line or within a glove box, using distilled and degassed water and

freshly concentrated ammonia solution made from bubbling NH_3 gas through likewise distilled and degassed water.

A green aqueous $[Fe(NH_3)_6]^{2+}$ solution was prepared by dissolving freshly prepared ammonium iron sulphate, $[(NH_4)_2Fe(SO_4)_2]\cdot 6H_2O$ (5 mmol), in H_2O (10 mL) and adding a concentrated ammonia solution (10 mL, 25 wt.%) in a Schlenk flask. An aqueous NCN^{2-} solution was prepared by dissolving molecular cyanamide H_2NCN (20 mmol) in H_2O (4 mL) and adding a concentrated ammonia solution (2 mL) in another Schlenk flask. Then, the mixture of both solutions of $[Fe(NH_3)_6]^{2+}$ and NCN^{2-} was stirred, after which the excessive ammonia was removed by applying a vacuum. After several minutes, a pale green crystalline solid **1** was formed. It was collected by filtration, washed with water and dried under vacuum. Yield: 60% with respect to $[(NH_4)_2Fe(SO_4)_2]\cdot 6H_2O$. Elemental analysis (%) calcd of **1**: C 17.42, H 1.46, N 40.63; found: C 17.22, H 1.97, N 40.76; IR (KBr): ν(NH) = 3290 (s); ν_{as}(NCN) = 2230 (s); δ(CNH) or ν_s-(NCN) = 1198 (m); δ(NCN) = 554 cm^{-1} (m).

A brown powder of **2** was prepared by the careful decomposition of **1** in a flux of LiCl/KCl (ratio: 46:54, mp. 352 °C) at temperatures between 390 and 410 °C under a protective argon atmosphere. The mixture was sealed in a glass ampoule (l = 30 cm) of which one half inside a tube furnace, whereas the other half was held at room temperature, just to allow the formation of pure melamine at the cold side of the glass container as a by-product. After cooling the ampoule to room temperature, the FeNCN could be washed with water and dried under vacuum. Elemental analysis (%) calcd of **2**: C 12.53, H 0, N 29.22; found: C 13.01, H 0.21, N 29.16; IR (KBr): ν_{as}(NCN) = 2127 (s); δ(NCN) = 645 cm^{-1} (s).

The powder X-ray diffraction data of $Fe(NCNH)_2$ (**1**) and FeNCN (**2**) were recorded at room temperature by means of a calibrated STOE STADI2/PL diffractometer with strictly monochromatized $Cu_{K\alpha 1}$ radiation and a linear position-sensitive detector (PSD) with a glass-capillary (0.3 mm diameter) sample holder; the range of measurement was 5–115° in 2Θ with individual steps of 0.01°. The X-ray powder diagrams were indexed using the WinXpow program. The primary structural models (atomic positions) were deduced by a comparison with the crystal structures of $M(NCNH)_2$[12] and MNCN[13] (M = Co, Ni). The backgrounds of the data sets were manually subtracted by linear interpolation, and the FULLPROF[20] program package was used for the Rietveld refinement with a pseudo-Voigt profile function. X-ray single-crystal measurements of FeNCN (**2**) were performed at 293(2) K using a Bruker SMART APEX CCD diffractometer with graphite-monochromatized $Mo_{K\alpha}$ radiation. After the usual data and empirical absorption corrections, SHELXL97[21] was used for the structure refinement.

Crystal data of **1**: $Fe(NCNH)_2$, M_r = 137.91, space group *Pnnm* (no. 58); a = 6.6705(4), b = 8.7840(4), c = 3.3302(1) Å, V = 195.13(2) Å^3, Z = 2; R_p, R_{wp}, R_{Bragg} = 0.009, 0.012, 0.18. Fe on 2*a*; N1 on 4*g* with x = 0.284(1), y = 0.532(1); N2 on 4*g* with x = 0.075(1), y = 0.7633(9); C on 4*g* with x = 0.161(2), y = 0.654(1); H on 4*g* with x = 0.756, y = 0.561 (not refined but riding on N1 with a fixed N1-H ≡ 0.86 Å as found in the isomorphous Co and Ni compounds[12]).

Crystal data of **2**: FeNCN, M_r = 95.88, space group $P6_3/mmc$ (no. 194); $a = b$ = 3.2689(2), c = 9.401(1) Å, V = 86.99(1) Å^3, Z = 2. The structure was refined by means of anisotropic displacement parameters for iron and isotropic ones for N and C. The final values for wR_2 (all data) and R_1 [$I > 2\sigma(I)$] were 0.131 and 0.055 for 6 parameters and 66 independent reflections. Fe on 2*a*; N on 4*f* with z = 0.3795(11); C on 2*c*.

More details about the crystal-structure investigation may be obtained from Fachinformationszentrum Karlsruhe, Germany (email: crydata@fiz-karlsruhe.de), on quoting the depository number CSD-No. 419222 for $Fe(NCNH)_2$ and CSD-No. 419223 for FeNCN.

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Keywords: carbodiimides · cyanamide · iron · magnetic properties · Rietveld refinement

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