

Article

Synthesis, Crystal Structure and Properties of Iron Bisdicyanamide ($\text{Fe}[\text{N}(\text{CN})_2]_2$) and Iron Diammin Bisdicyanamide ($\text{Fe}[\text{NH}_3]_2[\text{N}(\text{CN})_2]_2$)

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Abstract

The phase-pure syntheses of $\text{Fe}(\text{dca})_2$ and $\text{Fe}(\text{dca})_2(\text{NH}_3)_2$ have enabled comprehensive investigation of their structural and magnetic properties. $\text{Fe}(\text{dca})_2$ crystallizes in the orthorhombic space group $Pnmm$, with Fe^{2+} ions octahedrally coordinated by six dca ligands, forming a rutile-like 3D network. Temperature-dependent structural analysis reveals minor distortions and a slight unit cell volume contraction ($\sim 2.5 \text{ \AA}^3$) from 300 K to 25 K. $\text{Fe}(\text{dca})_2(\text{NH}_3)_2$ crystallizes in the monoclinic space group $P2_1/c$, featuring two axial ammonia ligands and dca-bridged Fe^{2+} ions forming layers. Magnetic susceptibility measurements of $\text{Fe}(\text{dca})_2$ reveal a ferrimagnetic transition at $T_C = 19.1 \text{ K}$, confirmed by SQUID data, Mößbauer spectroscopic measurements and low-temperature neutron diffraction. A magnetic hysteresis at 5 K indicates long-range cooperative magnetic ordering. ATR-IR spectroscopic measurements support the structural models and confirm the chemical composition of both compounds. TGA shows the thermal decomposition of $\text{Fe}(\text{dca})_2$.

Keywords: crystal structure; iron; dicyanamide; ammonia; magnetism; x-ray diffraction; neutron powder diffraction



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1. Introduction

The identification of molecular and solid-state structures has long been a central objective in chemistry and materials science, as structural elucidation is closely linked to the understanding and control of the physical and chemical properties of compounds. Such knowledge not only enables the rational tuning of material behavior but also provides a foundation for the design and development of tailored compounds with desired functionalities. While there is a large variety of well-known compounds containing oxides, compounds comprising nitrogen are comparably less often studied. In addition to the pseudo-chalcogenide cyanamide/carbodiimide moiety $(\text{NCN})^{2-}$ [1–10] and the guanidine

moiety (CN_3H_5) [11,12], the pseudo-halide dicyanamide ($(\text{N}(\text{CN})_2)^-$, dca) has been studied in the recent past. The boomerang-shaped dicyanamide unit has up to four coordination sites attributable to the free electron pairs at the $\mu 1$ -, $\mu 3$ - and $\mu 5$ -positions. Several dicyanamide-containing compounds are known, whose structure, physical and chemical properties have been investigated such as the 3D metal bisdicyanamides $M(\text{dca})_2$ with $M = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ [13–21].

One of the pure 3D metal bisdicyanamides, $M(\text{dca})_2$ with $M = \text{Fe}$, has already been investigated regarding its properties [15–17,19]. To date, its structure has not been conclusively determined, since a phase-pure synthesis has proven difficult to obtain [13,14,18]. In this work, we summarize previous findings on $\text{Fe}(\text{dca})_2$, provide a structural characterization and conduct further analyses of physical and chemical properties. Additionally, we synthesize and characterize $\text{Fe}(\text{NH}_3)_2(\text{dca})_2$, which is a compound of the $\text{ML}_2(\text{dca})_2$ type that has been already studied using different metals M and ligands L , such as $\text{Fe}(\text{C}_5\text{H}_5\text{N})_2(\text{dca})_2$ [22] or $M(\text{NH}_3)_2(\text{dca})_2$ with $M = \text{Co}, \text{Ni}$ [23], Cu [24]. While $M(\text{dca})_2$ -type compounds show a 3D structure, $\text{ML}_2(\text{dca})_2$ -type compounds are characterized by a layered structure. These layers are connected by π -stacking [22] or hydrogen bonds [23,24]. While the pure dicyanamides (without additional ligands) show cooperative magnetism at low temperatures [13,14,18], the compounds incorporating additional ligands are paramagnetic over the entire temperature range.

2. Results

In the following sections, we present the physical and chemical properties of $\text{Fe}(\text{N}(\text{CN})_2)_2$ (**1**) and $\text{Fe}(\text{NH}_3)_2(\text{N}(\text{CN})_2)_2$ (**2**), which we analyzed using X-ray and neutron diffraction, magnetic measurements (SQUID data), Mößbauer spectroscopy, thermogravimetric analysis (TGA), and infrared spectroscopy (ATR-IR).

2.1. Structural Description and Discussion

The structural data for **1** were derived from X-ray powder diffraction at 300 K and neutron powder (NP) diffraction at 25 K (Figure 1).

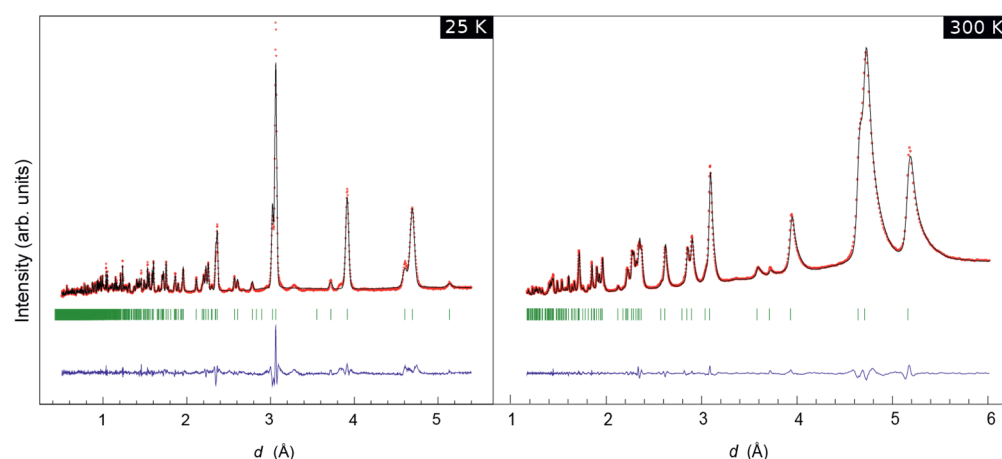


Figure 1. Rietveld refinements of **1** from NP data at 25 K (**left**) and from PXRD data at 300 K (**right**) with measured data in red, calculated patterns in black, reflection positions in green and difference curves in blue.

The magnetic structure is discussed in the *magnetic measurements* section and is based on the neutron powder data at 10 K, since the magnetic phase-change temperature is at $T = 19$ K. In the temperature range from 300 to 25 K, the compound crystallizes in the orthorhombic crystal system with space group $Pnmm$ (no. 58), and is, therefore, isostructural

to known transition metal bisdicyanamides [13,15–18,20,21]. At 25 K, the lattice parameters are $a = 6.0476$ (3) Å, $b = 7.1029$ (2) Å, $c = 7.4385$ (2) Å, $V = 319.52$ (2) Å³. At 300 K, they are $a = 6.0728$ (3) Å, $b = 7.1532$ (3) Å, $c = 7.4132$ (4) Å, $V = 322.03$ (3) Å³, with $Z = 2$. The lattice parameters are also summarized in Tables A1–A3. Six dca units surround each Fe²⁺ ion: four are equatorially coordinated at either their μ_1 or μ_5 position, forming chains made of Fe²⁺ ions connected via two dca units. The other two dca moieties are in *trans* position and are coordinated at the μ_3 position. Since such a dca moiety is basically part of another, yet similar chain that is, however, shifted and rotated corresponding to the bridging positions, the structure of **1** is a rutile-like 3D network. The coordination sphere of iron in **1** arising from the NP diffraction data refinement at $T = 25$ K is shown in Figure 2. At 25 K, the distances between the nitrogen and iron atoms are $d(\text{N1–Fe}) = 2.1316$ (19) Å and $d(\text{N2–Fe}) = 2.197$ (3) Å, leading to an almost perfect octahedron with the nitrogen atoms at the corner and the iron cations at the center. At 300 K, the distance between N2 and Fe increases ($d(\text{N2–Fe}) = 2.225$ (8) Å), while the distance between N1 and Fe decreases ($d(\text{N1–Fe}) = 2.095$ (5) Å). Thus, the octahedron is distinctly distorted in the a/c -direction (N1–Fe–N1-direction), which is also apparent from the lattice parameters.

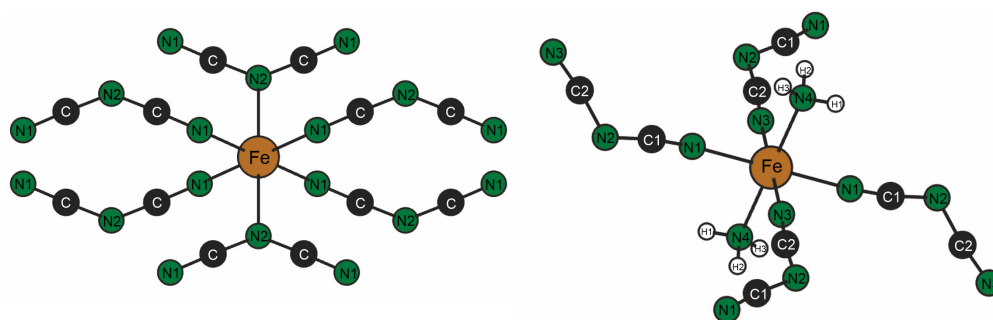


Figure 2. Coordination sphere of iron in **1** (left) and **2** (right) with iron in brown, carbon in black, nitrogen in green and hydrogen in white.

The lattice parameter c increases with decreasing temperature, while the lattice parameters a and, in particular, b decrease, resulting in an overall volume shrinkage of approximately 2.5 Å³ ($\Delta V_{300\text{K–}25\text{K}} = 0.8\%$). This volume contraction is comparatively small relative to that observed for the isostructural compound cobalt bisdicyanamide, for which the volume decreases by about 3 Å³ within a temperature range of only 170 K, which means that over a range, it is approximately 100 K smaller than that for **1**. In contrast, Zn(dca)₂ exhibits a significantly larger volume decrease of approximately 14 Å³ between 293 and 123 K. Furthermore, Ni(dca)₂ and Mn(dca)₂ show an increase in the lattice parameters a and c upon cooling. The origin of these differing thermal expansion behaviors among the binary 3D bisdicyanamides remains unclear, particularly because compounds containing nickel, manganese, and iron exhibit increasing lattice parameters with decreasing temperatures, whereas the cobalt and zinc analogs do not.

A comparison of the lattice parameters of the compounds at room temperature reveals a clear trend: as the atomic number of the 3D metals increases, the lattice parameters a , b and c decrease, along with the ionic radii r (Figure 3). Thus, this observation is in accordance with chemical intuition, and compound **1** conforms to this trend. The only exception in this series is the zinc phase, whose lattice parameters are significantly larger than those of the other 3D metals. The full 3D shell ($4s^0 3d^{10}$) of a Zn²⁺ ion could cause a significant increase in the lattice parameters.

The crystal structure of **2** (Figure 2, right) was determined at 300 K using X-ray powder diffraction (Figure 4, right). The compound crystallizes in the monoclinic space group $P2_1/c$ (no. 14) with the lattice parameters $a = 5.943$ (2) Å, $b = 10.8241$ (4) Å, $c = 6.8887$ (3) Å,

$\beta = 97.6035 (16)^\circ$, $V = 439.27 (3) \text{ \AA}^3$ and $Z = 2$. Similar to **1**, **2** comprises four equatorially coordinated dca units at either their μ_1 or μ_5 positions. However, they form chains by connecting Fe^{2+} ions via a single dca unit. Because each μ_1 and μ_5 position of a dca unit links different iron atoms, layers are formed. Additionally, each Fe^{2+} ion is coordinated at the *trans* positions by two ammonia groups (at the lone pairs of the nitrogen atoms) yielding a nearly perfect octahedral coordination with the six nitrogen atoms coordinating the iron. The hydrogen atoms of the ammonia groups form hydrogen bonds with the layers above and below, bonding, in particular, to the lone pairs of the nitrogen atoms of the dca units. The distances between the nitrogen atoms of the dca units and the Fe^{2+} cations are $d(\text{N}_{\text{dca}}-\text{Fe}) = 2.1194 (5) \text{ \AA}$ and between the ammonia nitrogen atoms and the Fe^{2+} cations are $d(\text{N}_{\text{NH}_3}-\text{Fe}) = 2.1500 (5) \text{ \AA}$. Further compounds are reported in the literature that contain central transition metal atoms coordinated by dicyanamide and ammonia ligands [23,24].

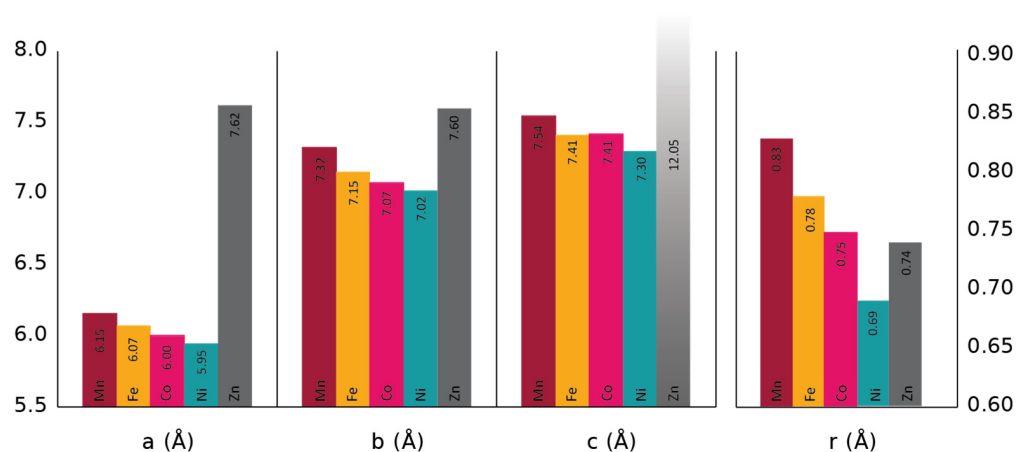


Figure 3. Lattice parameters and ionic radii of $M(\text{dca})_2$, $M = \text{Mn, Fe, Co, Ni, Zn}$ at room temperature.

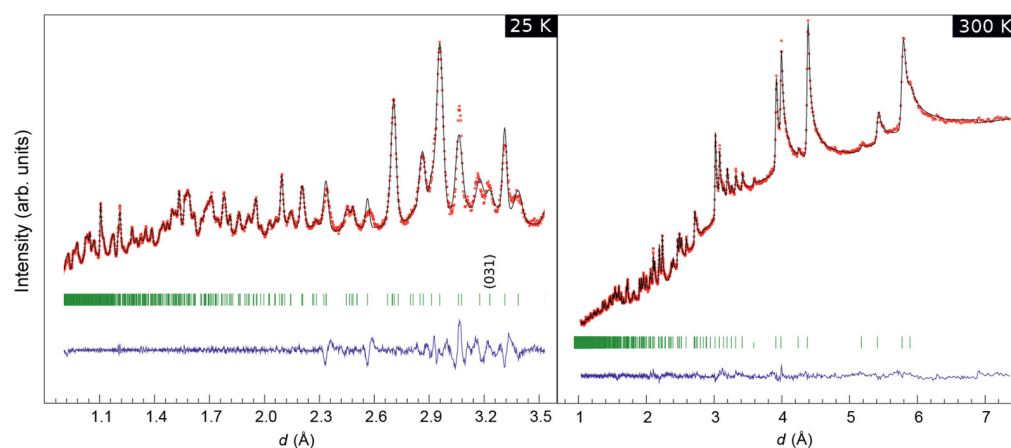


Figure 4. Rietveld refinement of **2** at 300 K from the X-ray powder data (**right**) and from the neutron powder data at 10 K (**left**) with measured data in red, calculated patterns in black, reflection positions in green and difference curves in blue.

For example, the compound **2** reported herein shows similar features to $\text{Co}(\text{dca})_2(\text{NH}_3)_2$ [23]; both were measured at $T = 300 \text{ K}$. Comparing the lattice parameters of both substances, all lattice parameters are larger in the case of the compound with cobalt as the central atom. The deviations of a , b , and β are less than 1%, while the deviation of c is 1.5%. Accordingly, the volumes of the two unit cells differ by 4%. Regarding the radii of the doubly positive transition metals, the trend of the lattice parameters is reversed: the radius of Co^{2+} is $r(\text{Co}^{2+}) = 0.56 \text{ \AA}$, while that of Fe^{2+} is $r(\text{Fe}) = 0.63 \text{ \AA}$, corresponding to a difference between the radii of 11%.

Beyond dicyanamide-based coordination compounds, further nitrogen-rich Fe(II) coordination compounds provide additional reference points for the coordination environment of compound **2**. For example, $[\text{Fe}(\text{H}_2\text{O})_4(\text{N}_5)_2] \cdot 4\text{H}_2\text{O}$ [25] also exhibits an octahedral Fe(II) coordination motif. While compound **2** features an all-nitrogen FeN_6 coordination sphere formed by dicyanamide and ammonia ligands, the Fe atom in $[\text{Fe}(\text{H}_2\text{O})_4(\text{N}_5)_2] \cdot 4\text{H}_2\text{O}$ is coordinated by two nitrogen and four oxygen donor atoms. Thus, the latter exhibits a more heterogeneous coordination environment, reflected by the different Fe–N and Fe–O bond lengths. In contrast, the six Fe–N distances in compound **2** are highly similar ($\Delta d = 0.03 \text{ \AA}$), indicating a highly regular FeN_6 coordination environment despite the presence of chemically different N-donor ligands.

To determine the hydrogen positions and anisotropic displacement parameters of **2**, the neutron diffraction data were refined using the crystal structure determined from X-ray diffraction at 300 K as the starting model (Figure 4, left). While the reflections at small d -spacings important for the refinement of anisotropic displacement parameters were reproduced satisfactorily, significant discrepancies were observed at larger values. In particular, the reflections at $d = 2.5, 3.0, 3.2$, and $3.3 \text{ \AA}$ could not be adequately fitted, although they are predicted by the structural model derived from the 300 K X-ray diffraction data.

Several approaches were explored to improve the refinement. First, a micro-strain model was introduced to account for possible lattice strain or structural defects; this, however, did not result in a significant improvement. In addition, the structural model reported for $(\text{Ni}(\text{NH}_3)_2(\text{dca})_2)$ [23], which already includes a micro-strain contribution in its refinement, was used as an alternative starting point after replacing the central nickel atom with iron; however, even this model did not result in an improved fit of the observed reflections. Finally, preferred-orientation corrections were included in the refinement, yet no satisfactory agreement between observed and calculated intensities could be achieved.

The origin of these discrepancies remains unresolved. Possible explanations include disorder or alternative orientations of the NH_3 groups and hydrogen atoms that are not adequately captured by the room-temperature structural model. Furthermore, local structural defects or short-range ordering phenomena may contribute to the observed intensity mismatches. Since none of the tested refinement strategies led to a satisfactory description of the diffraction pattern, the available neutron diffraction data may not provide sufficient information to uniquely determine the hydrogen positions and displacement parameters. Additional neutron diffraction measurements will, therefore, be required to clarify the structural model and resolve the origin of the observed discrepancies.

2.2. Magnetic Measurements

The magnetic data of **1**, normalized to a single Fe^{2+} center, are shown in Figure 5. At 0.01 T, the compound was measured in zero-field cooling (zfc) and field cooling (fc) mode due to the well-known occurrence of long-range magnetic ordering [14]. At 400 K, the value of $\chi_m T$ is $2.77 \text{ cm}^3 \text{ K mol}^{-1}$ (Figure 5a). This value is distinctly below the expected range, $3.2\text{--}4.1 \text{ cm}^3 \text{ K mol}^{-1}$, of an isolated high-spin Fe^{2+} center [26]. At decreasing temperatures, the values of $\chi_m T$ remain almost constant down to 100 K and slightly decrease to about 25 K, showing diverging values regarding both measurement modes with the lower values in fc mode. Upon further cooling, both series significantly increase and reach maxima at 15 K with 38 (zfc) and $176 \text{ cm}^3 \text{ K mol}^{-1}$ (fc) dropping off to 6.42 and $37.9 \text{ cm}^3 \text{ K mol}^{-1}$ at 2.0 K. At 5.0 K, the molar magnetization is characterized by a hysteretic loop (Figure 5a, inset). At the highest fields of $\pm 5.0 \text{ T}$, the magnetization reaches $\pm 0.8 N_A \mu_B$, while the coercive field is 0.5 T (horizontal intercepts at $\pm 0.47 \text{ T}$) and the remnant magnetization is $0.4 N_A \mu_B$ (vertical intercepts at $\pm 0.39 N_A \mu_B$). The shape of the $\chi_m T$ vs. T curve with decreasing temperatures from 400 K, and in particular below 100 K, is due to the thermal depopulation

of the energy states of the Fe^{2+} center split by electron–electron inter-repulsion, ligand field, and spin-orbit coupling. However, the magnetic properties of $\text{Fe}(\text{dca})_2$ are considerably affected by three-dimensional long-range ordering effects at even lower temperatures. This is evident from the observation of the hysteresis loop, the significant increase in $\chi_m T$ at about 25 K and the diverging $\chi_m T$ vs. T data in the zfc and fc measurement mode below that temperature. Such observations are characteristic of ferri- or ferromagnetic-phase transitions [26].

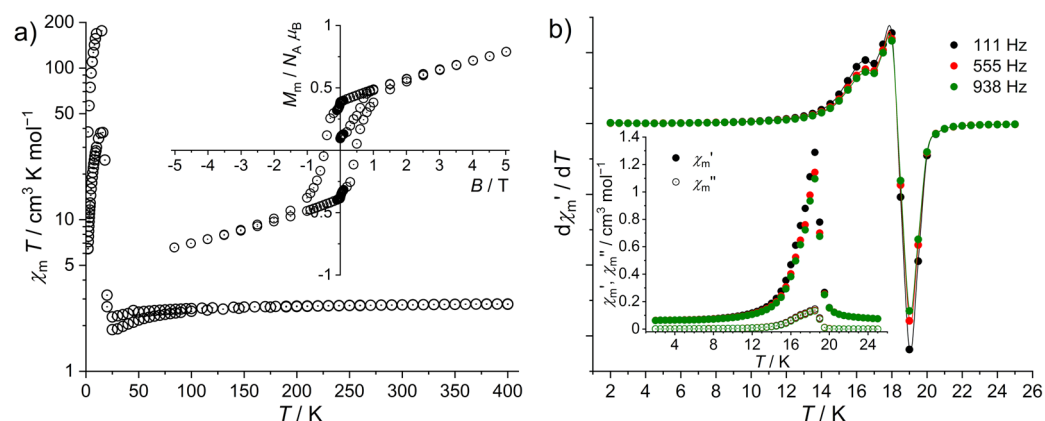


Figure 5. (a) Temperature dependence of $\chi_m T$ (zfc/fc) at 0.01 T of **1**; inset: molar magnetization M_m vs. applied magnetic field B at 5.0 K; and (b) temperature derivative of χ_m' vs. T for determination of the critical temperature T_C ; inset: corresponding in-phase molar magnetic susceptibility χ_m' vs. T and out-of-phase molar magnetic susceptibility χ_m'' vs. T at zero static magnetic bias field.

The $\chi_m T$ value at room temperature or even at 400 K, however, is distinctly below the value of an isolated high-spin Fe^{2+} center (and considerably above values of low-spin ($S = 0$) or intermediate-spin scenarios ($S = 1$)). This may indicate the presence of antiferromagnetic exchange interactions of lower dimensionality, although the slope of the $\chi_m T$ vs. T plot is rather small in this temperature range. A comparison with the literature [14] shows that we find slightly smaller values of $\chi_m T$ at room temperature. In addition, we find a distinctly lower coercive field and a broader width of the ac measurements data (see Figure 5b), which may indicate that **1** is a ferrimagnet instead of a canted antiferromagnet, as concluded by Kurmoo and Kepert [13]. **1** characterized as a ferrimagnet could also explain the rather low magnetization values at ± 5.0 T, since the saturation magnetization is expected to be a third of $4 N_A \mu_B$ ($\approx 1.3 N_A \mu_B$) in this case.

Additionally, the critical temperature T_C can be reliably determined from the minimum of the temperature derivative of the in-phase component (χ_m'). We find that $T_C = (19.1 \pm 0.1)$ K is in good agreement with the literature [14].

For gaining more insight into the magnetic structure of **1**, powder neutron diffraction data were obtained at 10 and 25 K to complement the conclusions and assumptions of the SQUID measurements. The results of these measurements are shown in Figure 6. If the difference between the two measurements at 10 K and 25 K is examined, the 10 K measurement shows two additional reflections at approximately 165,000 μs , two additional reflections at approximately 75,000 μs , which indicate antiferromagnetism, and higher reflection intensities at 85,000 and 70,000 μs , which indicate ferro- or ferrimagnetism. The appearance of the additional reflections at low temperature can be attributed to antiferromagnetic ordering, where the magnetic moments adopt a periodicity different from that of the crystallographic lattice. This enlarged magnetic unit cell results in additional magnetic superstructure reflections. In contrast, ferromagnetic or ferrimagnetic ordering does not necessarily lead to additional reflections but mainly manifests itself through changes in the intensities of existing Bragg peaks due to the magnetic contribution to the structure

factor. SQUID measurements distinctly prefer ferrimagnetism over ferromagnetism ($S = 2$). However, the additional reflections are too few to find a reasonable propagation vector for unambiguously determining the type of magnetism. Therefore, only an occurrence of cooperative magnetism can be confirmed along with a magnetic transition between 10 and 25 K, in agreement with the SQUID data.

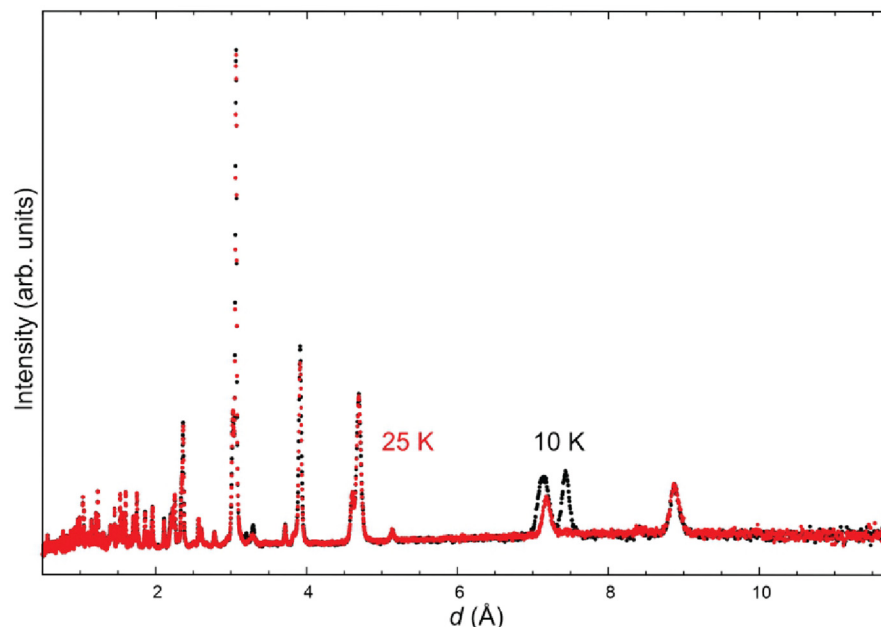


Figure 6. Powder neutron diffraction measurements of **1** at 10 K (black); and 25 K (red).

2.3. ^{57}Fe Mössbauer Spectroscopy

For **1**, the oxidation state of iron was investigated using ^{57}Fe Mössbauer spectroscopy. The ^{57}Fe Mössbauer spectrum of **1**, presented in Figure 7, shows a quadrupole split signal with an experimental line width of $0.35(1) \text{ mm s}^{-1}$ at an isomer shift of $1.12(1) \text{ mm s}^{-1}$, clearly indicating high-spin iron(II) [27]. Further examples for nitrogen-coordinated high-spin iron(II) compounds are $\text{Cs}_2\text{Fe}^{\text{H}}\text{Fe}^{\text{L}}(\text{CN})_6$ ($\delta = 1.040(5) \text{ mm s}^{-1}$ relative to $^{57}\text{Co}/\text{Pd}$ [MB3]), $\text{Fe}(\text{phen})_2(\text{NCS})_2$ ($\delta = 0.98(3) \text{ mm s}^{-1}$ relative to $\alpha\text{-Fe}$ [28]) and $[\text{Fe}(\text{btre})_2(\text{NCS})_2]$ ($\delta = 1.086(2) \text{ mm s}^{-1}$ relative to $^{57}\text{Co}/\text{Rh}$ [29]). The two crystallographically independent iron sites in the nitridosilicate $\text{Fe}_2\text{Si}_5\text{N}_8$ are also in a high-spin state with, however, slightly lower isomer shift values of $0.837(2)$ and $0.816(2) \text{ mm s}^{-1}$ [30].

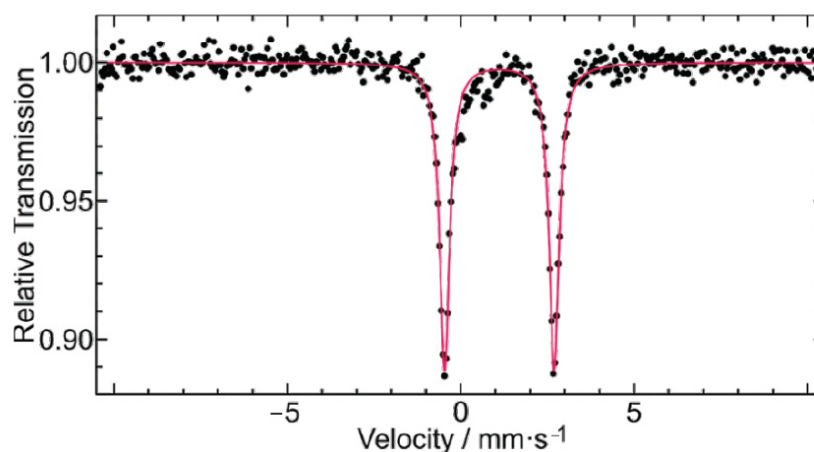


Figure 7. Experimental (data points) and simulated (colored line) ^{57}Fe Mössbauer spectrum of **1** measured at 78 K.

The significant quadrupole splitting of $3.16(1) \text{ mm s}^{-1}$ is a result of the coordination geometry of the iron atoms occupying Wyckoff site $2a$ (site symmetry $\cdot 2/m$). The iron atoms are coordinated by six nitrogen atoms in elongated octahedra ($4 \times \text{N1}$ at 209.7 pm and $2 \times \text{N2}$ at 221.7 pm); therefore, the N–Fe–N bond angles only slightly differ from ideal octahedral geometry (deviation equal or smaller than 0.8°). The elongation partially splits the degeneracy of the e_g and t_{2g} orbitals, which is reflected in the quadrupole splitting value.

At an isomer shift of around 0 mm s^{-1} , the experimental spectrum shows a very small additional contribution of an iron-containing impurity. The extremely low intensity prevents a sufficient fit; however, this does not interfere with the data of **1**.

2.4. ATR-IR and TGA

The ATR-IR measurements of **1** and **2** are shown in Figure 8 on the left. The results are in good agreement with those in the literature [18,23]. The allocated oscillations can be found in Table A2. Additionally, the oscillations for **1** and **2** were calculated with DFT, using a harmonic oscillation model to eliminate the overtones in the theoretical IR spectra (Table A4). It is notable that there is a signal at 2399 cm^{-1} in the IR spectrum of **1**, indicating water as an impurity, since the sample was stored under ambient conditions. The DFT calculations are in good agreement with the measurements.

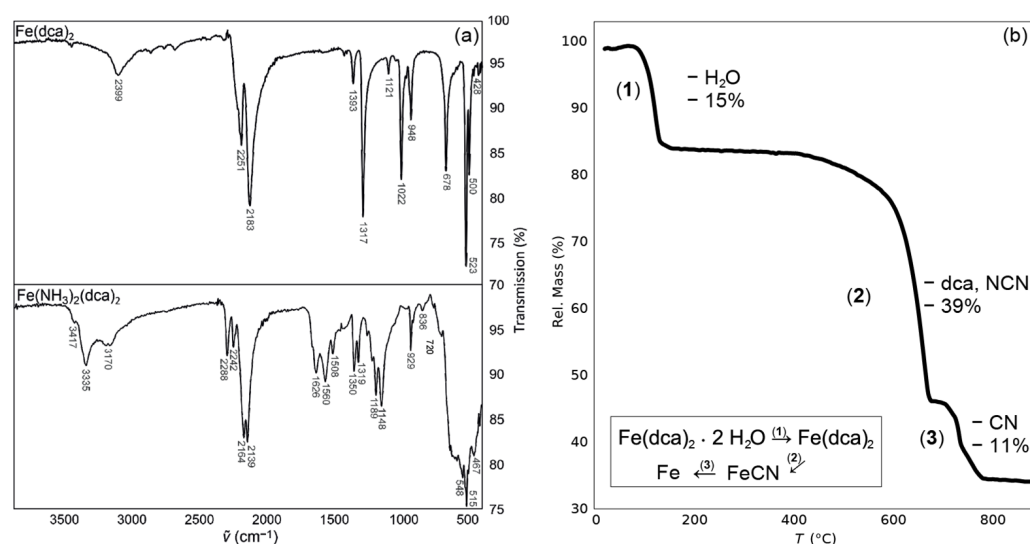


Figure 8. (a) ATR-IR measurements of **1** (top) and **2** (bottom); and (b) thermogravimetric analysis of **1** with possible decompositions steps (inset).

The results of the TGA of **1** are shown in Figure 7 on the right-hand side, plotting the mass fraction against the temperature. Three steps of mass loss occur at about $T \approx 120$ (1), 650 (2) and 720°C (3). Since the IR spectroscopic measurement revealed some water in the measured sample, the first step of mass loss (1) at $T \approx 120^\circ\text{C}$ is assigned to the cleavage of adsorbed water. A mass loss of approximately 15% corresponds to two water molecules per molecular unit Fe(dca)_2 , resulting in a molar mass loss of 36 g/mol . The subsequent mass loss (2) at $T \approx 650^\circ\text{C}$, from 85% to 46%, corresponds to a molar mass of about 92 g mol^{-1} . This loss could represent the sum of a dca and a NCN unit, in which case, a hypothetical iron–cyanide-containing residue remains. The final step of mass loss (3) occurs at about $T \approx 720^\circ\text{C}$, representing the cleavage of the remaining CN-containing species (46% to 35%) from the remaining iron-containing residue. We could not find a thermal decomposition of a “pure” transition-metal dicyanamide in the literature for comparison with our results; however, the cleavages of the above-described fragments seem reasonable. While the exact decomposition pathway remains uncertain, the proposed assignment provides the

best agreement with the observed mass-loss steps and is, therefore, considered the most plausible interpretation.

3. Materials and Methods

3.1. Synthesis

Fe(dca)_2 (**1**) was synthesized by adding a stoichiometric amount of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (3.96 g, 20 mmol) to a solution of NaN(CN)_2 (3.5615 g, 40 mmol, 2 equivalents) and H_2NCN (0.840 g, 20 mmol, 1 equivalent) in methanol. The solution was stirred for 1 h at room temperature. The product precipitated as beige microcrystalline powder. The powder was filtered, dried and prepared for powder X-ray diffraction. $\text{Fe(NH}_3)_2[\text{dca}]_2$ (**2**) was synthesized by recrystallizing **1** in liquid ammonia under Schlenk conditions: compound **1** (0.939 g, 5 mmol) was filled in a Schlenk flask and cooled to -78°C . Subsequently, ammonia was condensed into the flask while stirring the reaction mixture until all powder was suspended in the ammonia. In the next step, the excess of ammonia was removed by slowly thawing the solvents under standard conditions. The product was isolated as a black and sticky crystalline powder.

3.2. Powder X-Ray/Neutron Diffraction (PXRD/PND)

The compounds were measured on a Stoe STADI MP (STOE and Cie GmbH, Darmstadt, Germany) with $\text{Mo-K}_{\alpha 1}$ radiation ($\lambda = 0.709300 \text{ \AA}$) to avoid fluorescence and a Dectris Mythen2 1K detector. **1** was measured in a flat sample holder; **2** was loaded into a capillary with a diameter of 0.5 mm. Both samples were measured for 4 h in the $0\text{--}40^\circ$ transmission range, using Debye–Scherrer geometry.

Time-of-flight (TOF) powder neutron diffraction experiments were carried out at the Spallation Neutron Source (SNS) of Oak Ridge National Laboratory (ORNL) at the POWGEN powder diffractometer [31] to examine the crystal and magnetic structures of **1** and **2**. For measurements, powder samples of **1** and **2** were filled into vanadium cans with a 6 mm diameter. Background as well as vanadium corrections were applied using the standard data-reduction algorithm of POWGEN. The TOF experiments were carried out at 10 and 25 K with a neutron center-wavelength of $\lambda_c = 1.500 \text{ \AA}$, covering a d -range from 0.5 to $12.5 \text{ \AA}$ at 60 Hz.

3.3. Rietveld Refinements

Refinements of the data were made using the software *FullProf Suite* (Vers. 2023) [32].

(**1**): Fe(dca)_2 : For the powder X-ray diffractogram, the structural model of Co(dca)_2 was used, while cobalt was exchanged by iron. A pseudo-Voigt profile was used as the profile function. For the crystal structure refinement of the neutron powder data, the structure model obtained from the refinement of the powder X-ray diffractogram was used. Additionally, powder neutron diffraction experiments were performed at 10 K to find the possible magnetic peaks of the substance;

(**2**): $\text{Fe(NH}_3)_2(\text{dca})_2$: For the powder X-ray diffractogram, the structural model of $\text{Ni(NH}_3)_2(\text{dca})_2$ was used, while nickel was exchanged by iron. Since there were no magnetic structure changes observed between 10 and 25 K, the diffractogram at $T = 10 \text{ K}$ was refined because the isostructural compound $\text{Ni(NH}_3)_2(\text{dca})_2$ was measured at the same temperature, ensuring comparable results.

3.4. ^{57}Fe Mössbauer Spectroscopy

A $^{57}\text{Co/Rh}$ source was used for the Mössbauer spectroscopic characterization in conventional transmission geometry. A 75 mg amount of the $\text{Fe[N(CN)}_2]_2$ sample was mixed with alpha glucose and placed in a thin-walled PMMA container with a thickness

corresponding to about 7 mg Fe per cm². The measurement was performed in a commercial liquid nitrogen bath cryostat. The temperature of the absorber was set to 78 K, while the source was kept at room temperature. Fitting of the spectrum was performed with the WinNormos for Igor 8 program package [33].

3.5. Infrared Spectroscopy (ATR-IR)

The ATR-IR spectra (absorbance in dependence of the wavelength) were measured using a Bruker alpha II spectrometer (Bruker Optics, Ettlingen, Germany) and edited with the software OPUS (Version 7.8).

3.6. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of **1** was performed in a temperature range from 25 to 1000 °C with a heating rate of 5 K/min, while the compound was weighed using a Netzsch® STA 409 C (Netzsch, Selb, Germany). Due to the air sensitivity of compound **2** and the lack of an air-free transfer system to the TGA instrument, reliable measurements for this compound could not be obtained.

3.7. Magnetic Measurement

To determine the magnetic properties of **1**, measurements were performed with a Quantum Design SQUID Magnetometer MPMS-5XL. The crystalline powders were compacted and fixed in different PTFE capsules. Data were taken in dependence of the magnetic field (as hysteresis curve from −5.0 to 5.0 T at 5.0 K) and the temperature (field cooling (fc): 2.0 to 400 K with 0.01, 0.1 and 1.0 T, zero field cooling (zfc): 2.0 to 400 K with 0.01 T). Furthermore, measurements were conducted in a dynamic magnetic field with an amplitude of 3 T in the absence of a static magnetic field between 2.0 and 26.0 K and frequencies of $f = 111$, 555 and 938 Hz. All data were corrected for the diamagnetic contributions of the specimen holder and the intrinsic contribution of the sample ($\chi_{m,dia} = -9.4 \times 10^{-5} \text{ cm}^3 \text{ mol}^{-1}$).

3.8. Phonon Calculations

All structures were optimized using the Vienna Ab initio Simulation Package (VASP) [34–37] with the density functional theory (DFT). The electronic wave functions were derived from PAW pseudopotentials [38], employing a kinetic energy plane-wave cutoff of 500 eV. Exchange and correlation were GGA-parameterized according to Perdew–Burke–Ernzerhof optimized for solids (PBEsol) [39]. For the Brillouin zone integration, Blöchl’s tetrahedron method was employed, utilizing k-point meshes with densities ranging from 0.02 to 0.04 Å^{−1} [40]. Convergence criteria were set at energy differences of 10^{−4} eV Å^{−1} for ionic and 10^{−6} eV for electronic steps. To simulate lattice vibrations (phonons), Phonopy [41] was employed, utilizing the Hellmann–Feynman forces obtained from VASP. Furthermore, an in-depth simulation of infrared (IR) spectra was performed by employing phononic calculations and Born effective charges, which were also obtained through the aforementioned methods. The resulting data were meticulously processed using the JaGeo/IR software package (Version 1.0.4) [42].

3.9. Chemicals and Reagents

The following chemicals were used without further purification: FeCl₂·4H₂O (Merck KGaA, Schnelldorf, Germany, ≥99%), NaN(CN)₂ (Sigma-Aldrich, Schnelldorf, Germany, 96%), H₂NCN (Sigma-Aldrich, Schnelldorf, Germany, 99%), methanol (VWR Int., not given, 100%) and ammonia gas (Westfalen AG, Hörstel, Germany, 99.9999%).

4. Conclusions

Crystallographic and magnetic investigations of the iron-based dicyanamide compounds Fe(dca)_2 (**1**) and $\text{Fe(dca)}_2(\text{NH}_3)_2$ (**2**) were carried out. It is now finally possible to synthesize compound **1** in a phase-pure form, enabling more accurate and reliable characterization of its structural and magnetic properties. **1**, crystallizing in the orthorhombic space group $Pnmm$, forms a 3D rutile-like network with Fe^{2+} centers octahedrally coordinated by dicyanamide (dca) ligands. The structure exhibits only minor thermal contraction ($\Delta V \approx 2.5 \text{ \AA}^3$ from 300 to 25 K), in contrast to the larger volume changes observed in related compounds such as those of cobalt and zinc. The Fe–N bond lengths and lattice parameters show subtle but consistent temperature-dependent changes, suggesting slight octahedral distortion at higher temperatures.

In contrast, compound **2**, crystallizing in the monoclinic space group $P2_1/c$, forms a layered structure with Fe^{2+} centers, which are also octahedrally coordinated—by four dca ligands and two ammonia molecules. The hydrogen bonding from the ammonia groups plays a key role in stabilizing the layered network. The coordination geometry and bonding distances confirm nearly ideal octahedral symmetry. A comparison with similar cobalt-based analogues highlights predictable trends in lattice parameters corresponding to differences in the ionic radius.

The magnetic measurements of **1** demonstrate the complex behavior characteristic of ferrimagnetism, with a transition temperature $T_c \approx 19 \text{ K}$, as indicated by the SQUID data and neutron diffraction studies. ^{57}Fe Mössbauer spectroscopy confirmed the high-spin Fe^{2+} . Below the transition temperature, clear divergences in zfc and fc data and the emergence of hysteresis confirm the onset of long-range cooperative magnetism. The shape and temperature dependence of the $\chi_m T$ curve further supports a ferrimagnetic ground state with possible antiferromagnetic interactions at higher temperatures.

Thermal analysis of **1** shows a three-step decomposition process. The first mass loss at $T \approx 120 \text{ }^\circ\text{C}$ corresponds to adsorbed water, while further steps likely involve cleavage of dca and CN moieties, ultimately leading to iron-containing residues. The ATR-IR spectra and DFT-calculated vibrational modes corroborate the structural assignments and confirm the presence of water impurities.

In summary, the study of compounds **1** and **2** reveals the strong interplay between structure, temperature and magnetism in iron-based bisdicyanamides. The results deepen the understanding of structure–property relationships in this class of coordination polymers and highlight the influence of ligand type, metal ion and dimensionality on both crystallographic and magnetic behavior. Further investigations, however, are necessary to clearly determine the magnetic ordering in compound **1**. Further neutron diffraction experiments are needed to constrain and refine the proposed magnetic structure.

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(<https://www.ccdc.cam.ac.uk/mystructures/viewinaccesstructures/4140a0d7-8889-f111-96f0-00505695f620>, accessed on 14 August 2026) contain the crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, accessed on 14 August 2026 or from the CCDC, 12 Union Road, Cambridge CB21EZ; Fax: +44-1223-336033; E-Mail: deposit.ccdc.cam.ac.uk. All other data may be obtained from the corresponding author on reasonable request.

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Abbreviations

The following abbreviations are used in this manuscript:

dca	Dicyanamide
(P)XRD	(Powder) X-Ray diffraction
T.O.F	Time of flight
ATR-IR	Attenuated total reflectance-infrared spectroscopy
TGA	Thermogravimetric analysis
PND	Powder neutron diffraction
fc	Field cooling
zfc	Zero field cooling
SQUID	Superconducting quantum interference device
DFT	Density functional theory
GGA	Generalized gradient approximation
PBEsol	Perdew–Burke–Erzerhof (optimized for solids)
PAW	Projected augmented wave
VASP	Vienna Ab initio simulation package
SNS	Spallation Neutron Source
ORNL	Oak Ridge National Laboratory
N _A	Avogadro number
μB	Bohr magneton
μ1, μ3, μ5	Bridging modes of ligands
S	Spin quantum numbers
f	Frequency (Hz)

Appendix A

Table A1. Crystallographic data of the Rietveld refinement from the neutron powder data at 25 K and from the powder X-ray data at 300 K of paramagnetic iron bisdicyanamide (1).

	Neutron Data	X-Ray Data
T (K)	25	300
crystal system	orthorhombic	

Table A1. *Cont.*

	Neutron Data	X-Ray Data
Space group (no.)		<i>Pnmm</i> (58)
<i>a</i> (Å)	6.0730 (3)	6.0728 (3)
<i>b</i> (Å)	7.1536 (3)	7.1532 (3)
<i>c</i> (Å)	7.4137 (4)	7.4132 (4)
<i>V</i> (Å ³)	322.08 (3)	322.03 (3)
<i>Z</i>		2
$\rho_{\text{calc.}}$ (g/cm ³)	1.95	1.94
<i>U</i> , <i>V</i> , <i>W</i>	-	0.40 (11), 0.061 (30), 0.0021 (17)
<i>S_L</i> / <i>D_L</i>	-	0.028 (15)
η	-	0.8 (19)
<i>R_{Bragg}</i> , <i>R_F</i> , χ^2	5.79, 7.94, 36.0	3.18, 2.47, 36.9

Table A2. Crystallographic data of the Rietveld refinement from the neutron powder data at 10 K and from the powder X-ray data at 300 K of **2**.

	Neutron Data	X-Ray Data
<i>T</i> (K)	10	300
crystal system		monoclinic
Space group (no.)		<i>P2₁/c</i> (14)
<i>a</i> (Å)	5.8612 (15)	5.9434 (2)
<i>b</i> (Å)	10.803 (3)	10.8241 (4)
<i>c</i> (Å)	6.8014 (17)	6.8887 (3)
β (°)	96.270 (12)	97.6035 (16)
<i>V</i> (Å ³)	428.07 (19)	439.27 (3)
<i>Z</i>		2
$\rho_{\text{calc.}}$ (g/cm ³)	1.72	1.68
<i>U</i> , <i>V</i> , <i>W</i>	-	0.289 (4), −0.01 (4), 0.003 (5)
η	-	0.16761
<i>S_L</i> / <i>D_L</i>	-	0.0406 (2)
<i>R_{Bragg}</i> , <i>R_F</i> , χ^2	18.6, 12.7, 52.5	5.00, 4.12, 2.61

Table A3. Fitting parameters of the ⁵⁷Fe Mössbauer spectroscopic measurement for **1** at 78 K. δ = isomer shift, ΔE_Q = quadrupole splitting, Γ = experimental line width.

$\delta/\text{mm s}^{-1}$	$E_Q/\text{mm s}^{-1}$	$\Gamma/\text{mm s}^{-1}$
1.12 (1)	3.16 (1)	0.35 (1)

Table A4. IR data, measured and calculated, of **1** and **2** and the associated oscillations.

1 (Measured) $\tilde{\nu}$ (cm ^{−1})	1 (Calculated) $\tilde{\nu}$ (cm ^{−1})	Oscillation	2 (Measured) $\tilde{\nu}$ (cm ^{−1})	2 (Calculated) $\tilde{\nu}$ (cm ^{−1})	Oscillation
500	470	$\sigma_{\text{as}}(\text{N}-\text{C}\equiv\text{N})$	515	460	$\sigma_{\text{as}}(\text{N}-\text{C}\equiv\text{N})$
523	495	$\sigma_{\text{s}}(\text{N}-\text{C}\equiv\text{N})$	548	530	$\sigma_{\text{s}}(\text{N}-\text{C}\equiv\text{N})$
678	655	$\sigma_{\text{s}}(\text{N}=\text{C}=\text{N})$	720	720	$\sigma_{\text{s}}(\text{N}=\text{C}=\text{N})$
			836	752	$\gamma(\text{NH}_3)$
948	990	$\nu_{\text{s}}(\text{N}-\text{C})$	929	932	$\nu_{\text{s}}(\text{N}-\text{C})$
1022 *		* $\sigma_{\text{as}}(\text{N}-\text{C}\equiv\text{N})$			

Table A4. Cont.

1 (Measured) $\tilde{\nu}$ (cm ⁻¹)	1 (Calculated) $\tilde{\nu}$ (cm ⁻¹)	Oscillation	2 (Measured) $\tilde{\nu}$ (cm ⁻¹)	2 (Calculated) $\tilde{\nu}$ (cm ⁻¹)	Oscillation
1121 *		* $\sigma_s(\text{N}-\text{C}\equiv\text{N})$	1148 *		* $\sigma_s(\text{N}-\text{C}\equiv\text{N})$
			1189	1211	$\sigma_{as}(\text{N}-\text{C}\equiv\text{N}) + \sigma_s(\text{N}-\text{C}\equiv\text{N})$
1317	1310	$\nu_{as}(\text{N}-\text{C})$	1319 *		* $\sigma_s(\text{N}=\text{C}=\text{N})$
1393 *		* $\sigma_s(\text{N}=\text{C}=\text{N})$	1350	1388	$\nu_{as}(\text{N}-\text{C})$
			1508 *		
			1560	1556	$\sigma_{as}(\text{N}-\text{H})$
			1626 *		* $\gamma(\text{NH}_3)$
			2139 *		* $\nu_s(\text{N}-\text{C})$
2183	2275	$\nu_{as}(\text{N}\equiv\text{C})$	2164 *		* $\nu_s(\text{N}-\text{C})$
2251	2305	$\nu_s(\text{N}\equiv\text{C}) + \nu_{as}(\text{N}-\text{C})$	2242 *		* $\sigma_{as}(\text{N}-\text{C}\equiv\text{N}) + \sigma_s(\text{N}-\text{C}\equiv\text{N})$
			2288	2290	$\nu_s(\text{N}\equiv\text{C}) + \nu_{as}(\text{N}-\text{C})$
			3170 *		* $\sigma_{as}(\text{N}-\text{H})$
			3335	3300	$\nu_s(\text{N}-\text{H})$
3399 **		H ₂ O	3417	3390	$\nu_{as}(\text{N}-\text{H})$

* Overtone, ** Impurity.

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