Characterization of the Magnetic and Structural Properties of Copper Carbodiimide, CuNCN, by Neutron Diffraction and First-Principles Evaluations of Its Spin Exchange Interactions

Brian Barraza

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Characterization of the Magnetic and Structural Properties of Copper Carbodiimide, CuNCN, by Neutron Diffraction and First-Principles Evaluations of Its Spin Exchange Interactions

Xiaohui Liu and Richard Dronskowski*

Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, D-52056 Aachen, Germany

Reinhard K. Kremer and Martin Ahrens

Max Planck Institute for Solid State Research, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

Changhoon Lee and Myung-Hwan Whangbo

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204

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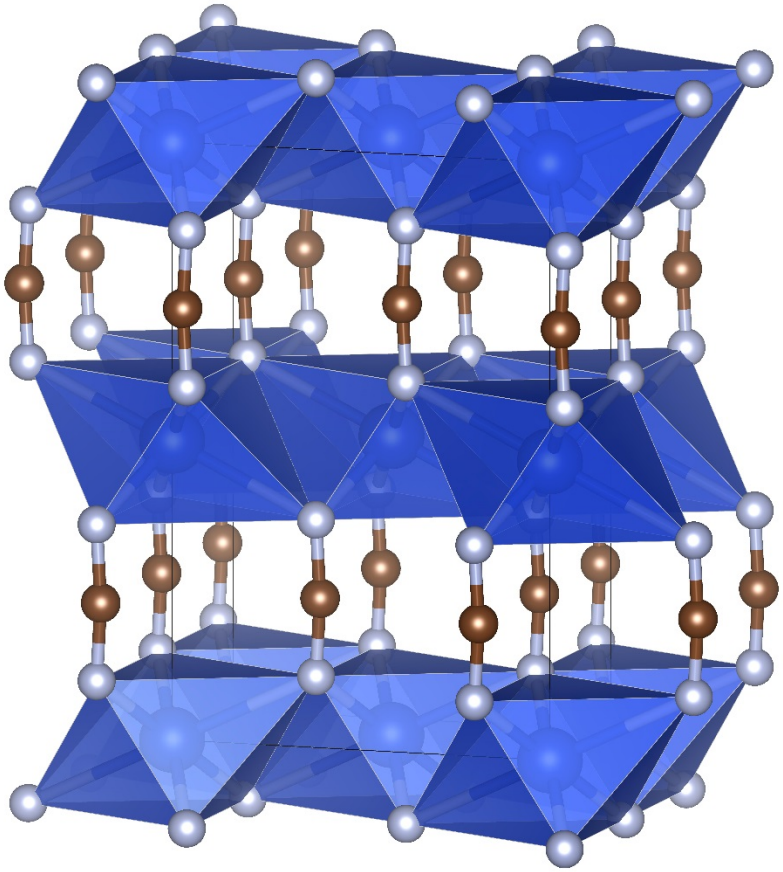
The crystal structure of copper carbodiimide, CuNCN, was determined from neutron diffraction data at room temperature and at 4 K, and the electrical resistivity, specific heat, and magnetic susceptibility measurements were carried out. The spin exchange interactions of CuNCN were evaluated by performing first-principles density functional theory electronic structure calculations. CuNCN is a semiconductor containing Jahn−Teller distorted CuN_6 octahedra around the divalent copper ions, and the material shows a very small and almost temperature-independent magnetic susceptibility. Our electronic structure calculations evidence that the spin exchange interactions of CuNCN are dominated by two antiferromagnetic spin exchange paths leading to a triangular lattice antiferromagnet within the *ab* plane. Because the coupling between the layers (along the *c* axis) is small, CuNCN may be regarded a two-dimensional $S = 1/2$ frustrated triangular Heisenberg quantum antiferromagnet.

Why CuNCN?

- Cu^{2+}: [Ar] $3d^9$
  - Paramagnetic transition-metal center
- NCN^{2-}
  - Diamagnetic bidentate bridging ligand

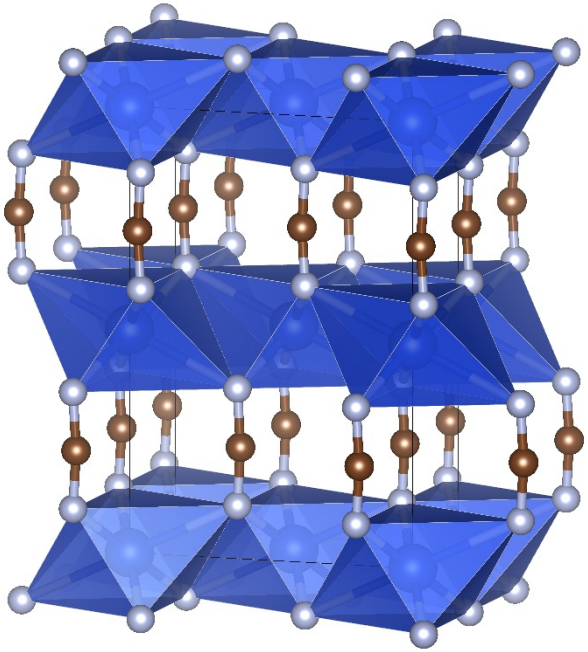
Magnetic Network Materials



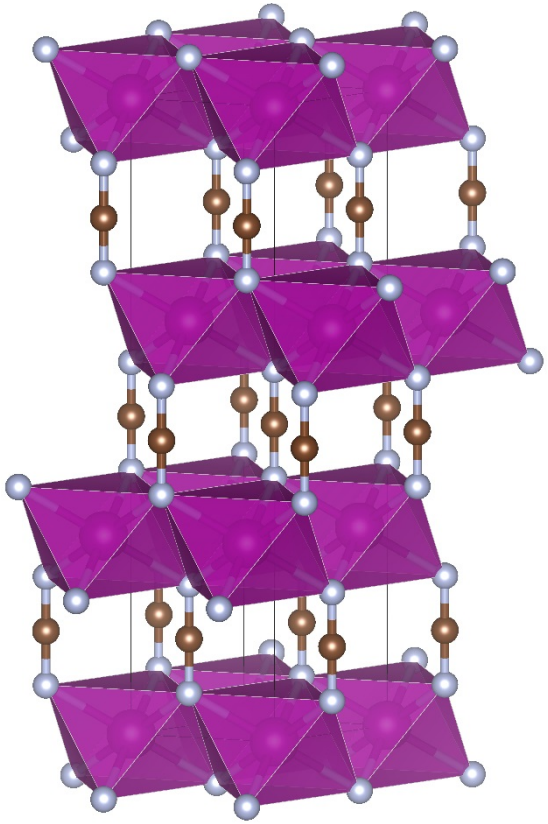
- Nitrogen analogues of metal oxides
  - $O^{2-} \rightarrow NCN^{2-}$
  - Much more spacious
- N-C-N^{o}
  - Small strain in angle allows for “wiggle room”
- Exhibit antiferromagnetic exchange interactions

Other NCN structures

CuNCN : C*mcm*

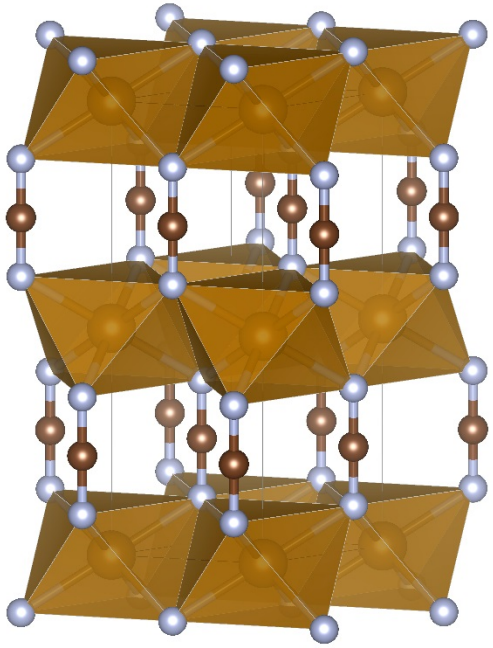


MnNCN : R3-*m*



Dronskowski, R. el al., *Inorg. Chem.* (2005) 44, (9) 3001-3003

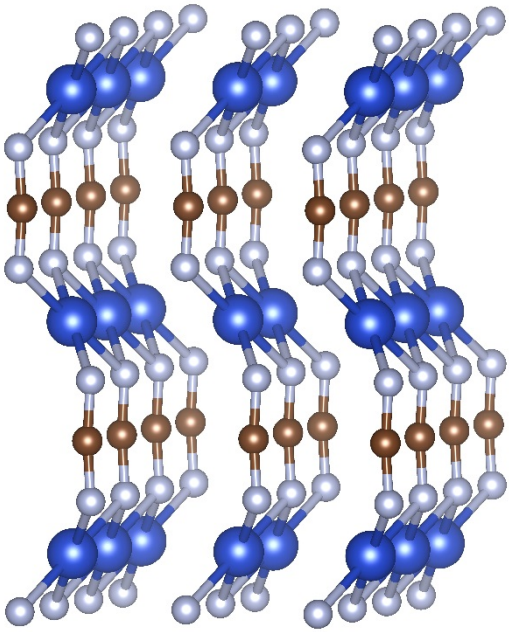
Fe, Co and NiNCN : $P6_3/mmc$



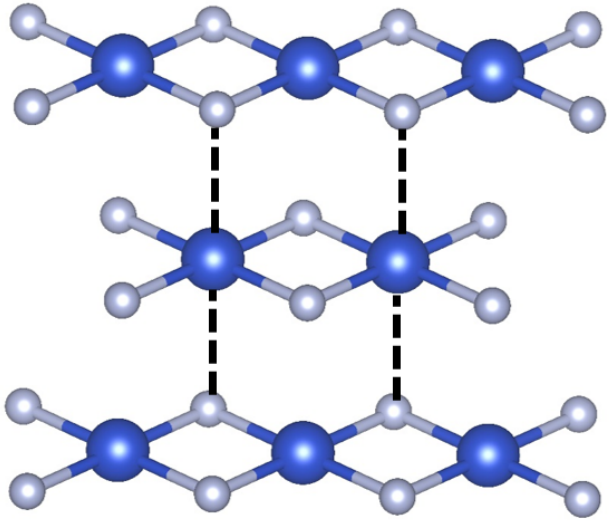
Dronskowski, R. el al., *Chem. Eur. J.* (2009) 15, (7) 1558-1561

Crystal Structure Determination

- Neutron Powder Diffraction at 4 and 293 K
  - At lower temp. unit of volume cell decreases
  - All bond angles and distances remain the same
  - NCN^{2-} angle is larger at lower temperatures, more linear



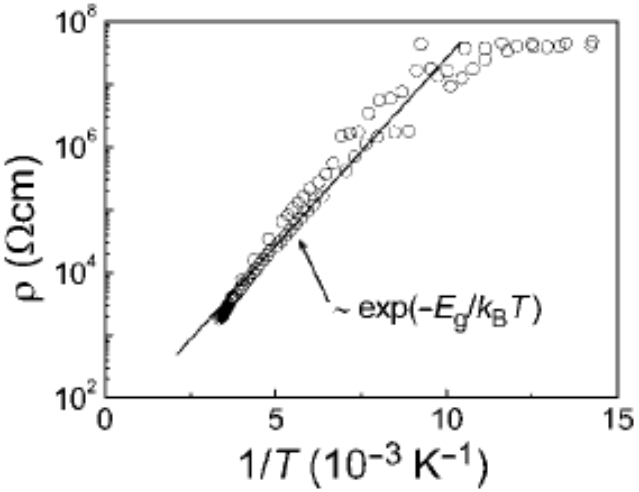
- Cu^{2+} ion
  - Coordinated to six nitrogen atoms
  - 4 short (2.0 Å) and 2 long (2.6 Å) Cu-N bonds
  - Jahn-Teller distorted structure
- Form corrugated sheets parallel to the ac plane



Electrical Resistivity

- Electrical resistivity of CuNCN was measured
  - Room temperature: semiconductor with a resistivity of about 1kΩcm
  - 100K resistivity levels of at 100 MΩcm.

6 orders of magnitude larger



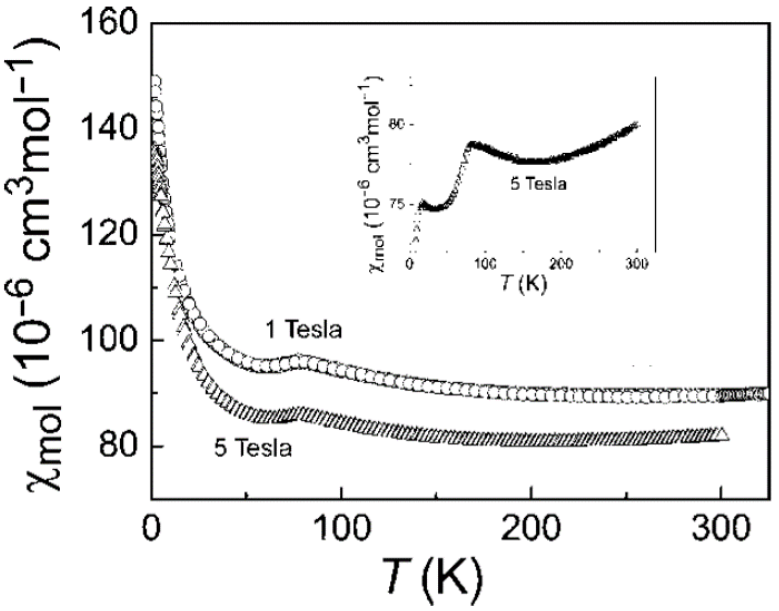
- Arrhenius plot shows an activation energy of the electrical resistivity
  - Fit of about 0.1 eV

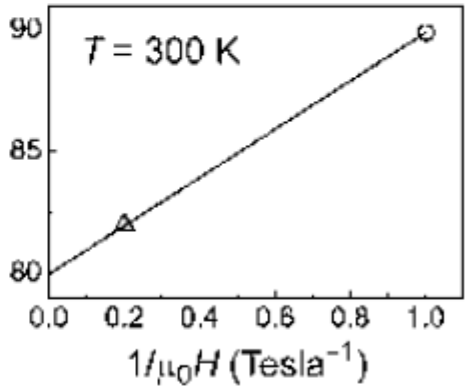
Magnetic Susceptibility of CuNCN

- Magnetic properties determined using a SQUID magnetometer.
  - Magnetic fields of 0.1, 1 and 5 T
  - Temperature (T) range: 1.85 K < *T* < 320 K

- Magnetic Susceptibility
  - Almost temperature independent
  - Slightly field dependent
- Increasing field *(H)* at 300 K
  - Paramagnetic value of about 80 X 10^{6-} cm^3/mol
- Below 50 K there is increase in susceptibility
  - Currie-Weiss contribution of $\chi = 6.1 \times 10^{-4} /(T-5K) cm^3 K mol^{-1}$

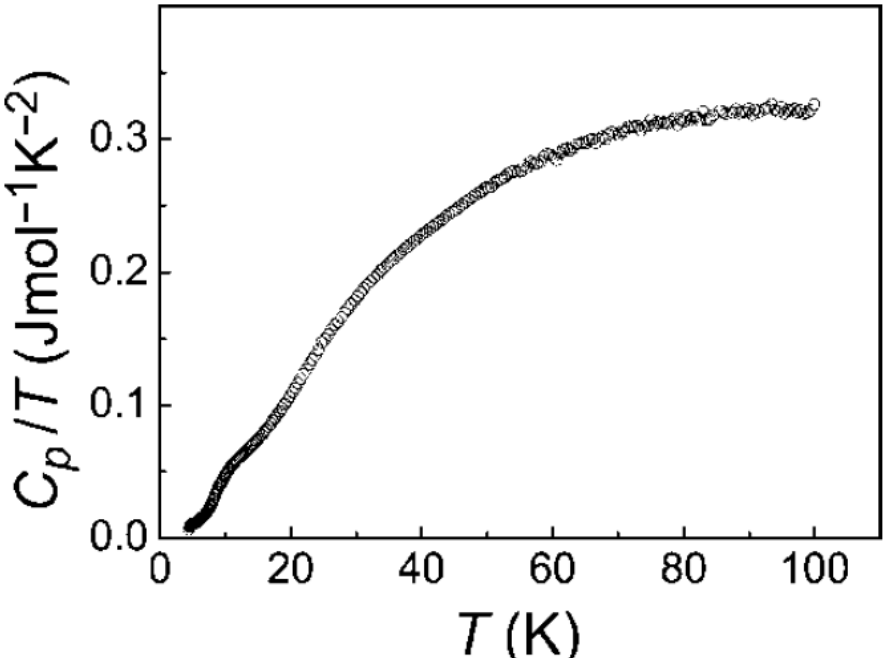
- Honda-Owen plot (χ) vs. (1/H)
  - Shows a hyperbolic decrease in susceptibility
  - Ferromagnetic impurities (Fe, etc…) 25ppm





Heat Capacity of CuNCN

- At 75 K and 0.1 T magnetic susceptibility measurements showed a broad maximum
- Heat capacity of CuNCN 4K-100K was taken
  - 0.2g Encapsulated in Duran glass under 1bar ^{4}He gas to enable thermal coupling
- No evidence for a magnetic phase transition below 100 K
- Anomaly at 10 K shows no relation to magnetic susceptibility measurements.

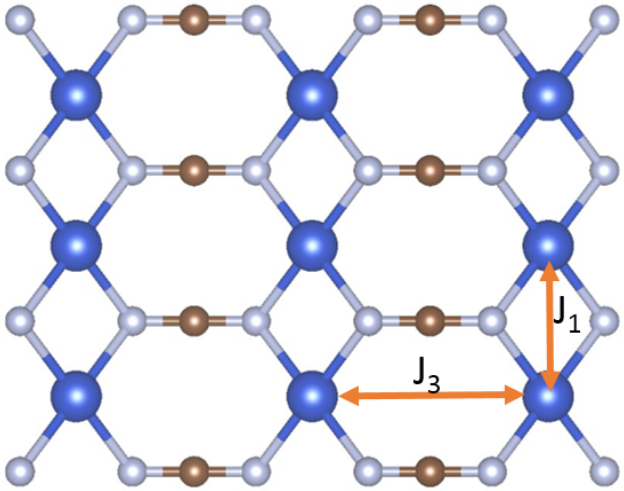


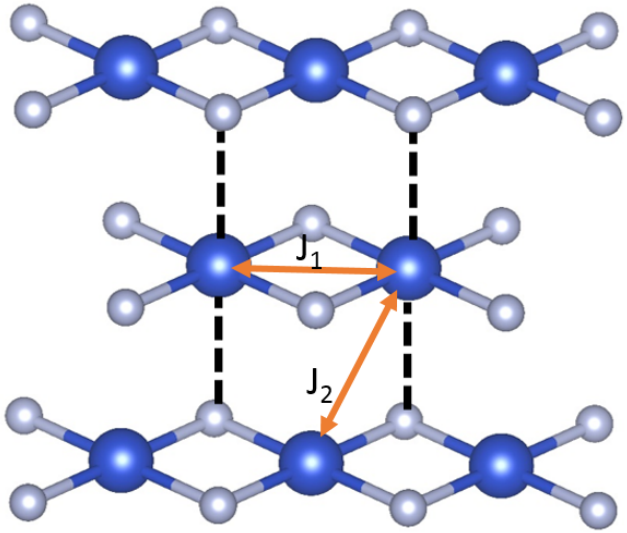
Spin Exchange Interactions

- Three spin exchange interactions
  - J_1, J_2, J_3
- This leads to four ordered spin states
  - FM, AF1, AF2, AF3
- Spin Hamiltonian used to determine energy differences

$$\hat{H} = -\sum_{i<j} J_{ij} \hat{S}_i \cdot \hat{S}_j$$

- J_{ij} = spin exchange parameter between spin states i and j
- $\hat{S}$ = spin angular momentum operator





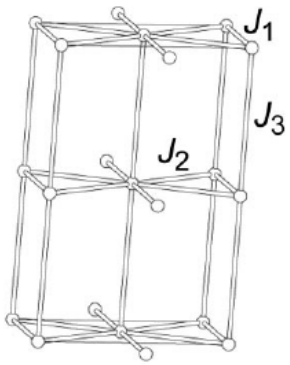
Spin Exchange Interactions

- The following expression can be used to describe the energies of the different spin states

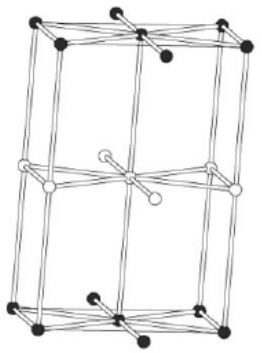
$$E_{FM} = (-4J_1 - 8J_2 - 4J_3)(N^2/4)$$
$$E_{AF1} = (-4J_1 - 8J_2 + 4J_3)(N^2/4)$$
$$E_{AF2} = (-4J_1 + 8J_2 - 4J_3)(N^2/4)$$
$$E_{AF3} = (+4J_1 - 4J_3)(N^2/4)$$

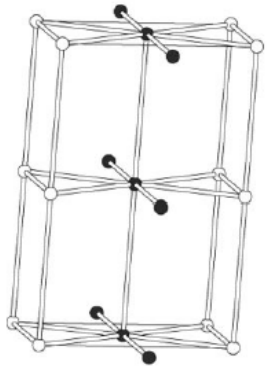
- N = unpaired spin (1)

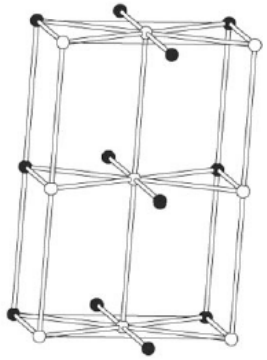
$$J_3 = (E_{AF1} - E_{FM})/(2N^2)$$
$$J_2 = (E_{AF2} - E_{FM})/(4N^2)$$
$$J_1 = (E_{AF3} - E_{FM})/(2N^2) - J_2$$



a) FM


b) AF1


c) AF2


d) AF3

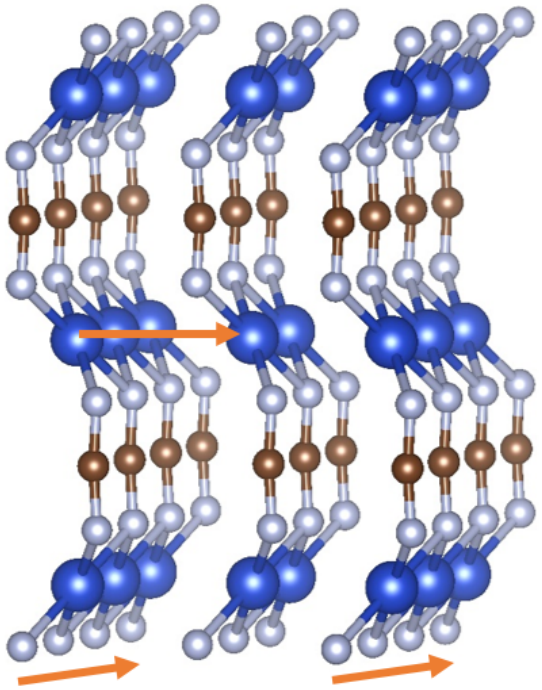
Spin Exchange

- DFT calculations found that spin exchange is dominated by J_1 and J_2 interactions. J_3 interaction are negligible

U (eV)	FM	AF1	AF2	AF3
4.0	0.0	0.31	−323	−297
6.0	0.0	−1.42	−457	−423

U (eV)	J_1	J_2	J_3
4.0	−67.8	−80.8	0.2
6.0	−97.1	−114	−0.7

  - Paths are observed within the ab plane, only.
  - Coupling between layers is small. Causes decoupling of layers
  - Creates a magnetism across the 2D plane
  - S= ½ frustrated Heisenberg quantum antiferromagnet (expected to have unusual quantum ground states).



Take Home Message

- CuNCN can be described as
  - Semiconductor at room temp
  - A magnetic insulator
  - Triangular lattice which leads to a highly correlated antiferromagnetic state.