



A unique copper coordination structure with both mono- and bi-dentate ethylenediamine ligands

Journal:	<i>CrystEngComm</i>
Manuscript ID	CE-ART-12-2018-002188.R2
Article Type:	Paper
Date Submitted by the Author:	25-Feb-2019
Complete List of Authors:	Sharma, Jai; University of Illinois at Urbana-Champaign, Materials Science and Engineering Jiang, Zhelong; University of Illinois at Urbana-Champaign, Materials Science and Engineering Bhutani, Ankita; University of Illinois at Urbana-Champaign, Materials Science and Engineering Behera, Piush; University of Illinois at Urbana-Champaign, Materials Science and Engineering Shoemaker, Daniel; University of Illinois at Urbana-Champaign, Materials Science and Engineering

Cite this: DOI: 10.1039/xxxxxxxxxx

A unique copper coordination structure with both mono- and bi-dentate ethylenediamine ligands

Jai Sharma,^{a†} Zhelong Jiang,^{a†} Ankita Bhutani,^a Piush Behera,^a and Daniel P. Shoemaker^{*a}

Received Date

Accepted Date

DOI: 10.1039/xxxxxxxxxx

www.rsc.org/journalname

The compound (ethylenediamine-N)-bis(ethylenediamine-N,N')-copper(II) bis(nitrate) is reported. It has an asymmetric unit containing Cu(II) penta-coordinating to two chelating ethylenediamine (en) and one monodentate en ligands with square-pyramidal-based geometry having severe trigonal distortion, together with two nitrate anions. It is the first crystallographic confirmation of the existence of penta-coordination with exclusively en ligands for any metal center, as well as the first monodentate en attached to Cu(II) seen in the solid state. It can be visualized as the penta-ammine effect realized solely with bi-amine ligands, defying the presumed necessity of mono-amines. X-ray crystallography establishes it to have P2₁/c space group with a = 12.83 Å, b = 9.77 Å, c = 11.91 Å, and $\beta = 94.8^\circ$ (at 100 K). Spectroscopic analysis of this compound is consistent with the crystallographic assessment of the coordination chemistry, and it is found to be a S=1/2 paramagnet.

1 Introduction

Ethylenediamine (en) is one of the most prevalent ligands in coordination chemistry and was once termed "God's gift to coordination chemist".¹ It is the most widely studied bidentate amine and readily forms highly stable five-membered metallocyclic rings when chelating a metal ion. Coordination compounds with en ligands and its derivatives are also used in the pharmaceutical²⁻⁴, agricultural⁵, polymer⁶, bleaching⁷ and industrial sectors⁸. The propensity of en to coordinate with metals also makes it a versatile reagent for the synthesis of inorganic materials through dissolution of metal salts or oxides, which can be engineered to precipitate in other crystalline forms.⁹⁻¹¹

Ethylenediamine is prevalently found to be bidentate. Monodentate or bridging forms of en are extremely rare.^{12,13} However, many kinetic intermediate species in a variety of important chemical processes have been proposed to contain complexes containing monodentate and bridging en with *trans* conformations. For instance, the ligand displacement reaction of a hexadentate cobalt(III) complex from EDTA⁴⁻ and PDTA⁴⁻ by en was rate-determined by the monodentate NH₂ coordination of the first en group.¹⁴ The isomerisation of the hydroxoammine complexes of cobalt(III) was found to involve unimolecular dissociation on one end of an en chelating ring.¹⁵ A monodentate en complex was

detected from the aquation of [*trans*-Cr(en)₂F₂]⁺, a low-lying σ -antibonding compound with important electron-transfer and photochemical characteristics.¹⁶ During the en-based solvothermal synthesis of magnetic chalcogenides KFeS₂ and KFe₂S₃, formation of Fe₂S₃ sheets connected by bridging en was suggested as the first reaction intermediate.⁹ However, these prior studies on monodentate en describe possible transient reaction intermediates, and the existence of monodentate en is only speculated upon based on spectroscopic evidence of solution-phase species. Only a few solid state compounds containing monodentate en have been crystallographically confirmed recently.¹⁷⁻²⁰ But in these examples, protonated enH is the actual monodentate ligand, and multiple ligands are involved in the metal coordination, so the steric and electronic effects are not entirely comparable to the case where en ligands are free to bond and dissociate.

In this paper, we report the crystallization and structure solution of (ethylenediamine-N)-bis(ethylenediamine-N,N')-copper(II) bis(nitrate) for the first time (Fig. 1). It is a penta-coordinated complex with two chelating and one monodentate en ligands with severely trigonally distorted square pyramidal stereochemistry. To the best of our knowledge, it is the first crystallographic confirmation for the existence of monodentate en when no other chemical species are introduced as mixed ligands. Such penta-coordination chemistry with en ligands has never been observed with any metal centers. The non-coordinating amine of this en is not protonated, and the N atom participates in hydrogen bonding to the amine H of a chelating en in the adjacent complex. It is also the first crystallographically characterized Cu

^a Department of Materials Science and Engineering, Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA. dpshoema@illinois.edu.

[†] These authors contributed equally to this work.

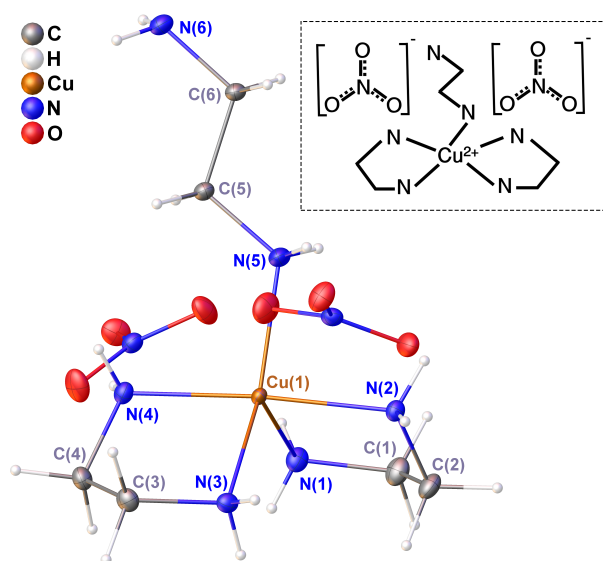


Fig. 1 Asymmetric unit of $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$. Anisotropic displacement ellipsoids (except H) are drawn at the 50 % level. The inset shows its chemical diagram. Cu(II) is coordinated to two bidentate en and one monodentate en in this structure.

ion coordinated to monodentate en. This unique coordination chemistry might originate from the penta-ammine effect. However, the penta-ammine effect is usually realized with five NH_3 ligands, or at least one mono-amine ligand is employed.²¹ Here, it is demonstrated that even with only the short bi-amine complex en, penta-amine coordination is still possible. Spectroscopic characterization of this compound supports the crystallographic assignment of square-pyramidal-based Cu(II)-tris(en) complex with penta-coordination. The insights from the stereochemistry of this complex are valuable to the analysis of reaction mechanisms and kinetics involving en ligands for coordination chemistry.

2 Experimental

2.1 Preparation of $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ single crystals

A solution of 50 mM $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with 33.3 vol% ethylenediamine was prepared by dissolving 0.1812 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in a mixture of 10 mL ethanol and 5 mL ethylenediamine. The resulting solution (15 mL) was placed in a 23 mL capacity PTFE-lined autoclave (Parr Instruments). The system was transferred into a preheated oven at 130 °C for 24 h. A homogeneous blue liquid was obtained after air-cooling the autoclave to room temperature, which was then transferred into a closed polypropylene centrifuge tube. Needle-shaped single crystals millimeters long in length formed from the liquid over a resting period of 24–72 h (Fig. 2).

Crystals of the same structure can be prepared without the solvothermal heating step. However, significantly increased single crystal precipitation rate and larger needles were observed with the solvothermal treatment.

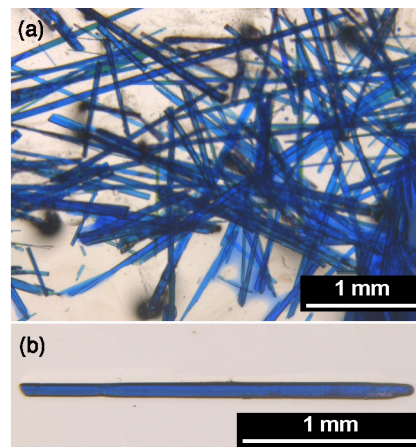


Fig. 2 Optical microscopy images of the blue needle-shaped $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ crystals.

2.2 Crystal structure determination of $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$

A suitable crystal was selected, chopped to proper length, and mounted on a Bruker D8 Venture diffractometer equipped with a Photon 100 detector using multilayer optics to monochromatize $\text{Mo K}\alpha$ radiation for single crystal diffraction. The crystal was kept at 100 K during data collection. Using Olex2²², the structure was solved with the ShelXT²³ using intrinsic phasing and refined with the ShelXL²⁴ refinement package using least squares minimisation. Additional refinement details and metrical parameters are provided in Table S1 in Supplementary Information.

2.3 Characterization

After precipitation of the crystals, inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed on the supernatant liquid using the PerkinElmer Optima 8300 to determine the Cu elemental concentration.

Heating or vacuum treatment will lead to structural changes of the crystals. Therefore, the powder samples used in the following characterizations were isolated from the liquid, dried at room temperature for solvent evaporation (sometimes with nitrogen gas flow) before performing the measurement. However, we expect some solvent molecules remaining adsorbed onto the crystals with such drying process (based on the mismatch of Cu ICP result of supernatant liquid and mass result of the dried precipitates). Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE diffractometer equipped with $\text{Mo K}\alpha$ source and LYNXEYE XE detector. Each sample was compacted inside a glass capillary and the diffraction was recorded in transmission configuration. Magnetic susceptibilities were recorded on a Quantum Design MPMS3 in the temperature range of 5–300 K under a magnetic field of 1000 Oe. The crystals were compacted into a cylindrical disc before magnetic measurement. Raman spectra were recorded using a Nanophoton Raman 11 confocal microscope with 532 nm laser excitation. Fourier transform infrared (FTIR) spectra of the crystals were collected on a Thermo Nicolet Nexus spectrometer in transmission mode. A 1 wt% sample pellet was made by mixing with KBr for FTIR measurement.

Diffuse reflectance ultraviolet-visible-near-infrared (UV-Vis-NIR) spectroscopy measurements were performed on a Varian Cary5G spectrometer. The sample crystals were placed on top of a BaSO₄ powder bed, with pure BaSO₄ powder used as reflection standard. The measured diffuse reflectance was converted to absorbance using the Kubelka-Munk transform.

3 Results and discussion

3.1 Crystallography

Blue needle-shaped single crystals precipitated from 50 mM Cu(NO₃)₂ ethanolic solution with 33.3 vol% ethylenediamine (en) days after solvothermal treatment (Fig. 2). The supernatant liquid after the precipitation of crystals was examined by ICP-OES to determine the Cu concentration. Based on the ICP-OES and density measurement results, it was calculated that at most 26% of the initial Cu elements was retained in the liquid. Therefore, the precipitation yield was at least 74% for this synthesis process in terms of Cu element.

Single crystal X-ray crystallography established monoclinic space group P2₁/c with lattice parameters $a = 12.8262(5)\text{\AA}$, $b = 9.7712(4)\text{\AA}$, $c = 11.9065(5)\text{\AA}$, and $\beta = 94.8220(10)^\circ$ at 100 K for the precipitated needles. The asymmetric unit consists of one mononuclear Cu(II) ion coordinated by three en ligands and two symmetrically inequivalent noncoordinating nitrate counter anions (Fig. 1). This renders its chemical formula of [Cu(en)₃](NO₃)₂. Detailed atomic coordinates and the anisotropic displacement parameters of the [Cu(en-N)(en-N,N')₂](NO₃)₂ crystal are provided in Table S2, S3, and S4 in the Supplementary Information. Powder XRD patterns for the precipitated crystals are provided in Fig. 3. As discussed in the caption of Fig. 3, the pristine crystals show very good agreement with the calculated powder XRD pattern based on its single crystal structure solution, but with the presence of preferred orientation, which is to be expected due to their needle shapes. Therefore, we conclude that our precipitates have good single-phase purity.

The coordination geometry of our crystal, however, is different from all copper tris(en) complex crystals known to date. Previously reported crystals containing [Cu(en)₃]²⁺ complexes are ubiquitously 6-coordinated with three chelating en ligands. For our crystal, the three en ligands coordinate differently: two en ligands are bidentate (chelating) as commonly found, but the third en ligand is monodentate, making this copper tris(en) complex 5-coordinated. Therefore, the proper name for this compound should be (ethylenediamine-N)-bis(ethylenediamine-N,N')-copper(II) bis(nitrate), with chemical formula of [Cu(en-N)(en-N,N')₂](NO₃)₂ to precisely reflect the uniqueness of this coordination structure.

This [Cu(en-N)(en-N,N')₂]²⁺ is penta-coordinated with distorted square pyramidal coordination geometry, with the chelating en donors at the four in-plane sites and the monodentate en donor at the apical site. Complete information on bond length and bond angles for [Cu(en-N)(en-N,N')₂](NO₃)₂ is listed in Tables S5, S6, and S7 in the Supplementary Information.

Bonds between Cu(II) and the N donors in the two chelating en have an average distance of 2.04 Å. Chelating en can bond

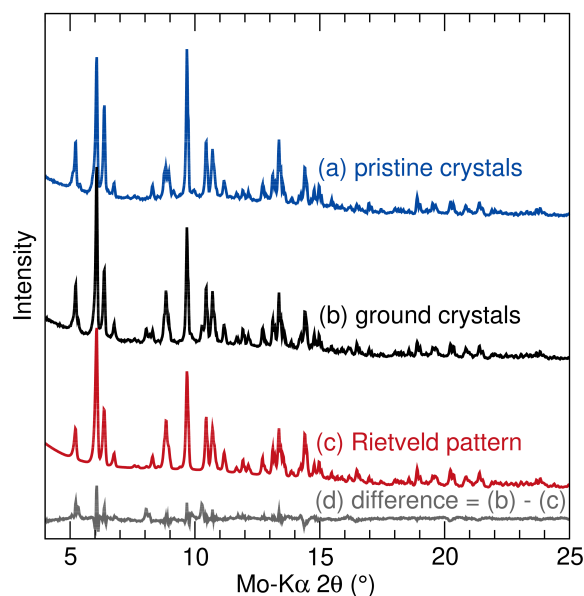


Fig. 3 (a) Powder XRD pattern taken by compressing the dried precipitate crystals directly into a glass capillary. (b) Powder XRD pattern taken by first grinding the dried precipitates before packing into the capillary. (c) Theoretical powder XRD pattern of [Cu(en-N)(en-N,N')₂](NO₃)₂ from Rietveld refinement on pattern (b). (d) The difference curve between (b) and (c). The ground sample (b) has no texture as compared to the needle-shaped crystals (a), which is preferred for Rietveld analysis (c). The major misfit peaks seen in (d) are not present in (a), so these misfit peaks are likely a consequence of grinding. Therefore, the pristine crystals are expected to be almost pure [Cu(en-N)(en-N,N')₂](NO₃)₂.

to central metal ions to form a five-membered puckered ring, with two possible enantiomeric conformations: λ and δ .¹ Our [Cu(en-N)(en-N,N')₂](NO₃)₂ is a racemate compound, with an equal mixture of $\lambda\lambda$ and $\delta\delta$ stereochemical forms.

The apical Cu(II)-N bond to the monodentate en has a longer bond distance of 2.21 Å. This disparity in bond distances is largely a consequence of the structural distortion originating from the 3d⁹ electronic configuration of Cu(II) (commonly present in penta-coordinated Cu complexes). This has similar underlying principle as the Jahn-Teller distortion in octahedrally coordinated structures with axial elongation.²⁵ This complex, therefore, is more accurately depicted as having "4+1" coordination, with a tetragonality T^5 of 0.923.^{1,26}

The square pyramidal geometry of [Cu(en-N)(en-N,N')₂]²⁺ is significantly trigonally distorted. One pair of the trans *in-plane* ligand donors bends away from the apical bonds ($\angle \text{N}(1)-\text{Cu}(1)-\text{N}(3) = 105.7^\circ$), whereas the other pair of trans *in-plane* donors remains relatively straight ($\angle \text{N}(2)-\text{Cu}(1)-\text{N}(4) = 175.5^\circ$). The geometry index τ_5 can be used to describe such in-plane angular distortion.²⁷ The τ_5 value for [Cu(en-N)(en-N,N')₂]²⁺ is calculated to be 0.464, almost at the midpoint between perfect square pyramid ($\tau_5=0$) and trigonal bipyramid ($\tau_5=1$).

When trying to view the structure as trigonal bipyramid, the two axial bonds have the shortest distances, with each chelating en contributing one N donor (N(2) and N(4)). The Cu-N bond for monodentate en is longer than the other two equatorial bonds,

which is a common consequence of distortion from perfect trigonal bipyramid.

The full list of hydrogen bonding for $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ is provided in Table S8 in the Supplementary Information, which is visualized in Fig. 4 for a single asymmetric unit. Most of the hydrogen bonding interactions are between hydrogens in $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2]^{2+}$ and oxygens in $(\text{NO}_3)^-$. The only exception is the dotted green lines in Fig. 4 that connects adjacent $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2]^{2+}$ complexes along the b-axis and involves the non-coordinating N(6) as the acceptor. This hydrogen bond is relatively short and straight. Its H-A distance is 2.204 Å, one of the shortest H-bonds in this structure, and its D-H-A angle is 164.0°. In fact, for the monodentate en, the coordination bond length (N donor to Cu: 2.21 Å) is almost the same as the hydrogen bond length (N acceptor to H: 2.20 Å). Therefore, this hydrogen bonding with N(6) is expected to have decent strength, which could weaken the Lewis basicity of N(6) and stabilize the monodentate en ligand.

3.2 Structural comparison with other complexes

A penta-coordinated tris(ethylenediamine) complex as seen in our $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ has never been crystallographically confirmed before. In the absence of an overriding factor, a complex containing chelating five-membered metallocyclic rings is expected when en or N,N-substituted en derivatives are employed as ligands.²⁸ Bridging and monodentate forms of en are extremely rare. The early postulations of their existence mainly came from spectroscopic inference on liquid solutions of complexes, and are thus less reliable.^{12,13,29,30} Only very recently have a handful of monodentate and bridging en compounds been confirmed crystallographically.¹⁷⁻¹⁹

$[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ differs from the other monodentate-en ligand compounds in three key aspects. First, no ligands other than en are present, whereas mixed-ligands donors are introduced in other examples to compete for chelating en ring formation through steric and electronic effects. Second, our $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2]^{2+}$ has a coordination number of 5, whereas all other examples have coordination number 6. Third, the monodentate en ligand in $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ is neutral, whereas in other structures mono-protonation occurs on the non-coordinating N of the monodentate en ligand.

Crystals with Cu(II) centers have never been reported with monodentate en, although an abundance of crystals containing Cu(II)-bis(en) and Cu(II)-tris(en) have been studied.³¹⁻³⁸ Our compound differs from the other 5-coordinated $[\text{Cu}(\text{en})_2\text{X}]^{2+}$ complexes in two key aspects. First, the basal plane in our $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2]^{2+}$ has severe trigonal distortion whereas the others are fairly flat. Second, the apical coordination bond in $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2]^{2+}$ is not semi-coordinating as in the others with ≥ 2.5 Å bond lengths.³⁹ As a reference, for elongated octahedral $[\text{Cu}(\text{en})_3]^{2+}$, the axial Cu-N lengths are mostly within the range of 2.3–2.4 Å. The mean apical Cu-N distance for a monodentate ligand, with the inclusion of all ligands besides en, is 2.263 Å in 4+1 coordinated complexes.⁴² Our Cu-N distance (2.21 Å) is even smaller than the above values, which confirms

that this monodentate en is indeed strongly coordinating.

The two chelating rings adopting the racemate $\lambda\lambda$ and $\delta\delta$ conformation (as in $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$) is very rare. Although a few exceptions exist,^{40,41} most Cu-bis(en) complexes adopt the $\delta\lambda$ form. In the solution phase, $\lambda\lambda$ (or $\delta\delta$) arrangement is estimated to be more stable (4 kJ mol⁻¹) than $\delta\lambda$ due to the -NH₂ protons having staggered configuration rather than eclipsed. But in the solid state, $\delta\lambda$ dominates due to crystal packing forces,^{1,31-34}

Perhaps the nearest comparable stereochemistry to $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2]^{2+}$ is the penta-ammine-Cu(II) complex as found in $[\text{Cu}(\text{NH}_3)_5](\text{PF}_6)_3$.²¹ In general, five-coordination of Cu(II) is hard to realize without mixed-ligands or π -bonding donors so as to introduce the possibility of bond-length and bond-angle distortion. However, NH₃ are known to exhibit a strong tendency to form CuN₅ chromophores with only σ -bonding, a phenomenon termed the penta-ammine effect. However, these penta-amine complexes typically uses ammine ligands, sometimes in combination with tetradentate / bidentate amine (such as $[\text{Cu}(\text{tren})(\text{NH}_3)](\text{ClO}_4)_2$ and $[\text{Cu}(\text{en})_2(\text{NH}_3)](\text{BF}_4)_2$).²¹ The use of ammine has been required to form the fifth coordination site on top of the characteristic 4 coordination of Cu(II).⁴³ It is unprecedented to achieve the penta-ammine effect with only one type of ligand that is fundamentally bidentate as is the case in our $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2]^{2+}$.

The extent of trigonal distortion ($\tau^5 = 0.464$) in $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2]^{2+}$ is also unforeseen in other 4+1 coordinated $[\text{Cu}(\text{en})_2\text{X}]^{2+}$ (X = other monodentate ligands) or $[\text{Cu}(\text{NH}_3)_5]^{2+}$ complexes where nearly regular square pyramids are universally adopted. Although it has comparable basal and apical Cu-N distances with our $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2]^{2+}$, penta-ammine $[\text{Cu}(\text{NH}_3)_5](\text{PF}_6)_3$ only has $\tau^5 = 0.022$.

The formation of this unique $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ can be examined as an intermediate between known complexes. The previously known Cu(II)-en complex with nitrate counterions is $[\text{Cu}(\text{en-N,N}')_2](\text{NO}_3)_2$.³¹ We synthesized this compound pure when ≤ 10 vol% en is employed. Our structure is a tris(en) complex, and with certain counter-anions (e.g. acetate, oxalate, chloride, sulfate), crystalline $[\text{Cu}(\text{en-N,N}')_3]^{2+}$ forms when the en to Cu(II) ratio is in excess of 3:1 in an aqueous environment.^{35,36,44} However, no $[\text{Cu}(\text{en-N,N}')_3]^{2+}$ has been reported in the solid state with nitrate. Our preliminary tests show that excess en prohibits crystallization. No crystalline precipitation will occur if en is ≥ 75 vol%. In this state, Cu(II) ions are expected to be present in the solution phase as $[\text{Cu}(\text{en-N,N}')_3]^{2+}$, but crystallization of their solid state equivalence with nitrate anions is forbidden for some reasons unclear.

The ideal en concentration for crystalline $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ formation should be larger than required for $[\text{Cu}(\text{en-N,N}')_2](\text{NO}_3)_2$, but not in excess to fully stabilize solution $[\text{Cu}(\text{en-N,N}')_3]^{2+}$. Within this range, the Cu-complexes in solution are speculated to be square-planar $[\text{Cu}(\text{en-N,N}')_2]^{2+}$, with some en ligands in solution available to contribute to further coordination.⁴⁵ The existence of a stable 5-coordinated Cu complex with tris(en) ligands in solution, as is found in our solid state example, is highly unlikely due to the incompatibility of

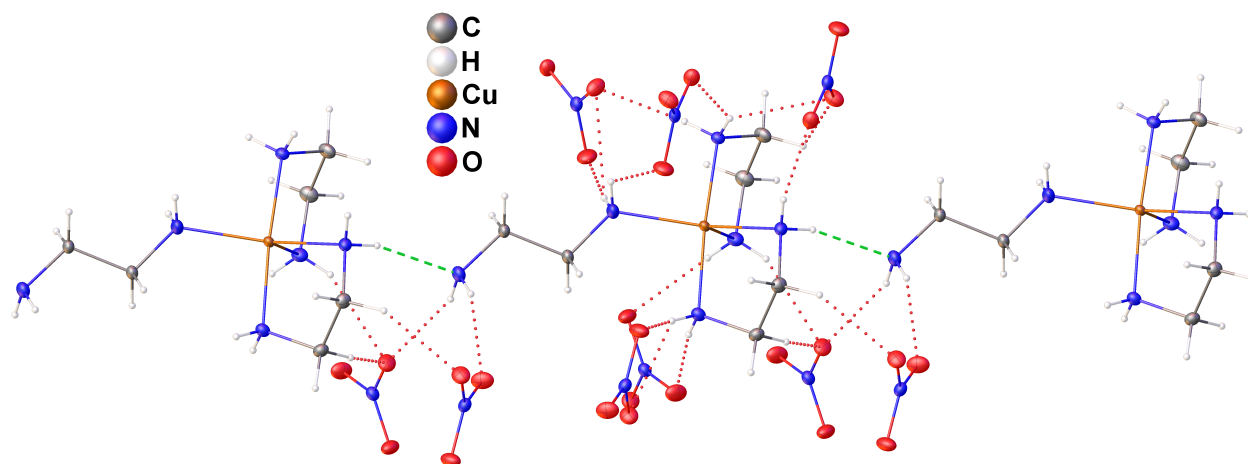


Fig. 4 Hydrogen bonding in $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ crystal. Hydrogen bonds between $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2]^{2+}$ and nitrate are shown with dotted red lines. The hydrogen bonds between N(6) (*i.e.* the non-coordinating en N) and H(3A) in adjacent $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2]^{2+}$ complexes along b-axis are highlighted as thickened green dotted lines.

fast exchange dynamics in the liquid phase with the extreme structural distortion caused by such stereochemistry. We postulate that Cu(II) was initially present in the solution as $[\text{Cu}(\text{en-N,N}')_2]^{2+}$, and during its condensation into solid state phase, the additional free en ligands participated in coordination by forming a fifth monodentate bond, achieving the penta-amine analog. This hypothesis is supported by the $\delta\delta$ and $\lambda\lambda$ ring conformations in $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2]^{2+}$, which are uncommon in solid state, but are more stable in the solution phase. The non-coordinating N in the monodentate en is partially stabilized through H-bonding, as demonstrated in Fig. 4. In the end, an equilibrium between $[\text{Cu}(\text{en-N,N}')_2]^{2+}$ in solution and $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2]^{2+}$ in solid state is achieved. This is in agreement of our observation that the liquid phase after precipitation remained blue, and the existence of significant amount of Cu in liquid from ICP-OES.

With insufficient en (*e.g.* 10 vol% en), we found that the liquid changed from blue to colorless after precipitation, and we confirmed the violet-colored precipitates to be pure $[\text{Cu}(\text{en})_2](\text{NO}_3)_2$ powder through XRD. On the other extreme, when excess en was used (≥ 75 vol% en), no precipitates can be found. A schematic for this proposed formation of $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ is shown in Fig. 5.

In our example synthesis using 50 mM $\text{Cu}(\text{NO}_3)_2$ with 33 vol% en, the en to Cu molar ratio was 100:1, far in excess of the 2:1 to 3:1 range we postulated. The addition of ethanol has been shown to induce crystallization of amine-based coordination compounds.⁴⁶ Therefore, the presence of ethanol might have an effect on reducing the effective number of en as ligands.

3.3 Spectroscopy and magnetism

Raman spectra of $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ crystal and pure liquid en are shown in Fig. 6. Modes of en have been assigned by Krishnan and Plane based on their study of en in water and heavy water.⁴⁵ Compared with their results, peaks in our en Raman spectrum are slightly shifted, probably due to the exclusion of wa-

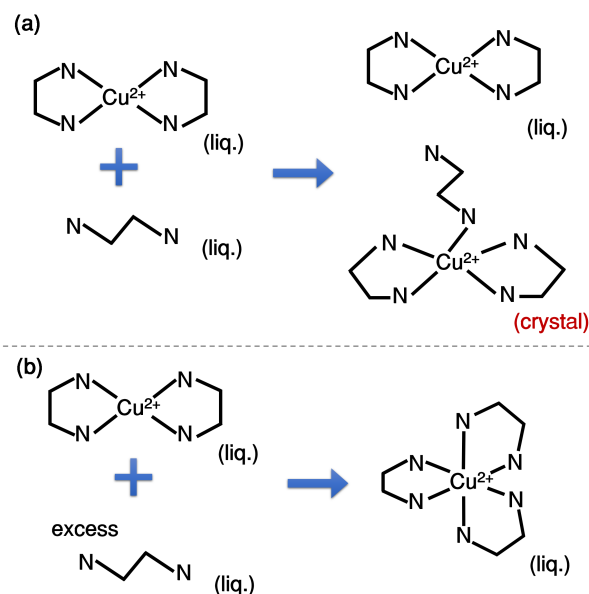


Fig. 5 Proposed formation scheme of $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ crystals. With insufficient en (≤ 10 vol% en), only $[\text{Cu}(\text{en})_2](\text{NO}_3)_2$ precipitates. (a) In the ideal condition of 33 vol% en and 67 vol% ethanol, Cu(II) ions are first coordinated with two chelating en ligands, with some free en ligands in the solution. Over time, the fifth coordination bond forms between some $[\text{Cu}(\text{en})_2]^{2+}$ and the free en, resulting in the precipitation of $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ crystals. (b) When there is excess en in the liquid (≥ 75 vol% en), stable octahedral $[\text{Cu}(\text{en})_3]^{2+}$ will form in solution, preventing the crystallization of $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$. $\text{Cu}(\text{NO}_3)_2$ concentration is fixed at 50 mM pertaining to the above discussion.

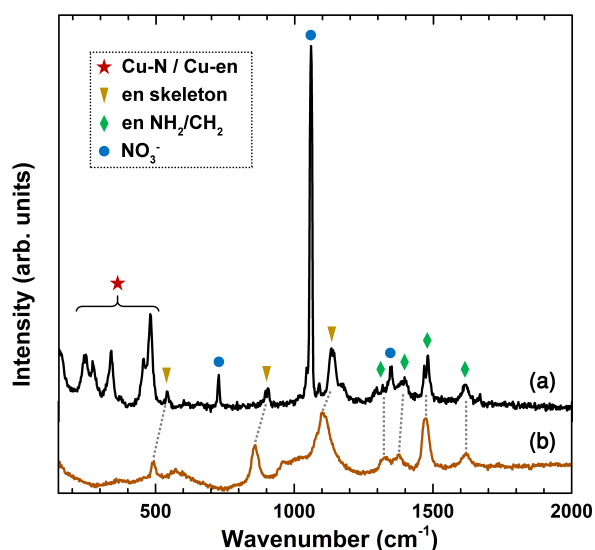


Fig. 6 Raman spectra of (a) $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ crystal and (b) liquid en. The Raman spectrum of $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ contain peaks corresponding to NO_3^- , en (wavenumber shifted compared to liquid en), and the Cu-tris(en) penta-coordination.

ter, but the overall pattern is consistent. Therefore, the following Raman-active vibration modes are suggested in Fig. 6(b): skeletal bending at 494 cm^{-1} , stretching at 858 cm^{-1} ; C–N stretching at 1100 cm^{-1} and 1020 cm^{-1} (shoulder peak); CH_2 twisting at 1328 cm^{-1} , bending at 1474 cm^{-1} ; and NH_2 twisting at 958 cm^{-1} , wagging at 1379 cm^{-1} , and bending at 1620 cm^{-1} . The Raman spectrum of the $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ complex seen in Fig. 6(a) has the modes originating from en shifted, which is to be expected due to en coordinating to metal ions.⁴⁵ As indicated in Fig. 6, the extent of peak shifts, however, are different depending on the vibrating atoms. Modes of CH_2 (twisting at 1317 cm^{-1} , bending at 1480 cm^{-1}) and NH_2 (wagging at 1396 cm^{-1} , bending at 1614 cm^{-1}) are observed with minimal shifts, whereas those corresponding to the en skeleton (bending at 541 cm^{-1} , stretching at 903 cm^{-1} , C–N stretching at 1132 cm^{-1}) have appreciable positive shifts. This can be appreciated considering that liquid en can freely transform between its trans and gauche(A,B) conformations⁴⁷, but once within the solid state complex, this freedom disappears and the molecule is markedly stiffer. The freedom of CH_2 and NH_2 vibrations, on the other hand, is not severely restricted by complex formation. Castro and Jagodzinski isolated three fundamental Raman peaks of NO_3^- with cation-insensitive positions.⁴⁸ All these three nitrate Raman modes are present in $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$, with very narrow peaks at 726 , 1059 , and 1346 cm^{-1} .

Low energy vibrations (less than 500 cm^{-1}) are generally associated with metal-donor coordinations. Five such strong Raman peaks can be easily identified for $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ in Fig. 6(a) at 245 , 271 , 339 , 456 , and 479 cm^{-1} . Generally, lower wavenumber modes are assigned to metal-nitrogen bending and higher wavenumber modes to metal-nitrogen stretching.⁴⁵ Critically, M–N stretching at *ca.* 420 cm^{-1} has been consistently observed in the tris(en) complexes of different metal ions, which

is not the case for $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$. This agrees with our crystallographic analysis that our tris(en) complex is 5-coordinated rather than the usual octahedral geometry for other compounds. The M–N stretching mode for known bis(en) complexes with two chelating rings appear at 450 cm^{-1} , which is close to the ones in $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$, consistent with this structure also having two chelating rings. Usually, only two major Raman peaks can be located within this wavenumber region for metal-en coordination, but five are identified here. This may be attributed to unique 5-coordination, making the Cu(II) center lack point symmetry. Although more precise assignment of the Raman modes for $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ was not made, Fig. 6 foretells which Raman spectral features can be expected from species having similar stereochemistry.

Fourier-transform infra-red (FTIR) spectrum of $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ is shown in Fig. S1 in the Supplementary Information. As is labeled in Fig. S1, it shows peaks arising from en ligands, superimposed with very strong peaks due to the presence of nitrate ions. The wavenumber and relative strength of these peaks agree well with other reports on en-containing complexes^{45,49–51}, and nitrate anion systems⁴⁸. This is consistent with our discussion on its Raman spectrum that vibration modes within such high wavenumber region originate from NO_3^- , CH_2 and NH_2 groups, and that such vibration modes are insensitive to the exact coordination stereochemistry. Some overlapping peaks between Fig. 6(a) and Fig. S1 can be identified that are both Raman and infrared active. Detailed assignment for the FTIR peaks are provided in Table S9 in the Supplementary Information.

The UV-Vis-NIR spectrum of $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ is presented in Fig. 7. It has a broad visible light absorption peaked at *ca.* 555 nm and extends to the NIR region. The absorption maximum correlates with the first coordination sphere in the complex.⁵² The 555 nm absorption maximum for our 5-coordinated $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ is in between the 514 nm seen in $[\text{Cu}(\text{en})_2]^{2+}$ and 609 nm in $[\text{Cu}(\text{en})_3]^{2+}$.^{52,53} A second smaller peak maximum in the NIR at 914 nm can be identified for $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ as well. This Vis-NIR spectrum agrees with the one observed in the square-pyramidal penta-ammine compound $\text{K}[\text{Cu}(\text{NH}_3)_5][\text{PF}_6]_3$, which has a primary peak maximum at 654 nm and a secondary one at 909 nm .²¹ Based on molecular-orbital analysis using extended-Hückel calculations, Duggan *et al.* showed that for square-pyramidal $[\text{Cu}(\text{NH}_3)_5]^{2+}$, the primary visible absorption was due to $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transitions, the secondary NIR absorption was due to $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions, and there was a weak band due to $d_{xy} \rightarrow d_{x^2-y^2}$ at 714 nm which could be resolved from the primary peak with Gaussian analysis.^{21,54} The same electronic transition assignment can be adopted for $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ (Fig. 7) due to the close resemblance in Vis-NIR spectra and stereochemistry. However, Cu(II) in $[\text{Cu}(\text{NH}_3)_5]^{2+}$ exhibits C_{2v} symmetry, whereas the Cu in $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2]^{2+}$ is at a general C_1 position. Therefore the degeneracy between d_{xz} and d_{yz} is expected to be lifted for our complex. Nevertheless, the energy separation between these two levels is small, with no readily-observable features (Fig. 7). Discussions on Cu(II) electronic levels based on crystal field theory are more prevalent,^{43,55,56} but are less applicable due to the lack of sym-

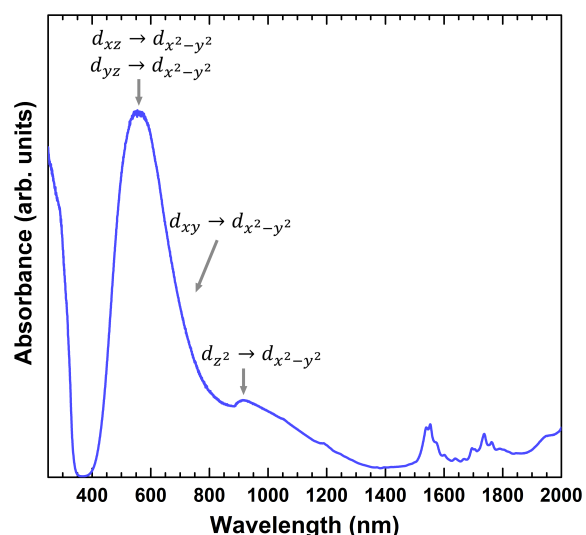


Fig. 7 UV-Vis-NIR spectrum of $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ crystals. The strong visible absorption peak at 555 nm with the NIR shoulder at 914 nm is consistent with square-pyramidal-based Cu-amine coordination.

metry in our complex.

The magnetic susceptibility measurement of $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ is shown in Fig. 8. It showed paramagnetic behavior at all measured temperatures which follows Curie's Law. The perfect overlap between zero-field-cooled and field-cooled curves demonstrates no remnant magnetization in this compound. Paramagnetism is expected in this structure since the magnetic Cu(II) ions are far from each other (closest Cu–Cu distance is 6.83 Å).

Based on the Curie constant derived from linear regression of the data over the temperature range of 5–200 K, the effective moment for the magnetic center was calculated to be 1.64 Bohr magneton (μ_B). Because of expected solvent molecules being adsorbed onto the crystal, the measured sample mass should be an overestimate. Therefore the calculated 1.64 μ_B is a low bound for the effective moment per Cu(II) center, consistent with the theoretical effective moment of 1.73 μ_B for a pure spin-1/2 system.

4 Conclusions

A new coordination crystal $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ is presented. Its Cu(II) ions are penta-coordinated to two chelating and one monodentate en ligands. The coordination structure of this crystal is particularly unique in the following ways. (1) It is the first crystal with penta-coordination containing monodentate en using exclusively en ligands. (2) It is the first crystal with Cu coordinated to a monodentate en ligand. (3) It has severe trigonal distortion to the basal square pyramidal stereochemistry. (4) It is an uncommon racemate Cu crystal with $\delta\delta$ (and $\lambda\lambda$) en chelate ring conformations. (5) Its non-coordinating en amine N is not protonated but H-bonded to chelating amine H atom in the adjacent complex. (6) It realizes the penta-ammine effect with only bi-amine ligands. The unique coordination chemistry of $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ is corroborated by spectroscopic analysis. Magnetic susceptibility indicates that it is a S=1/2 para-

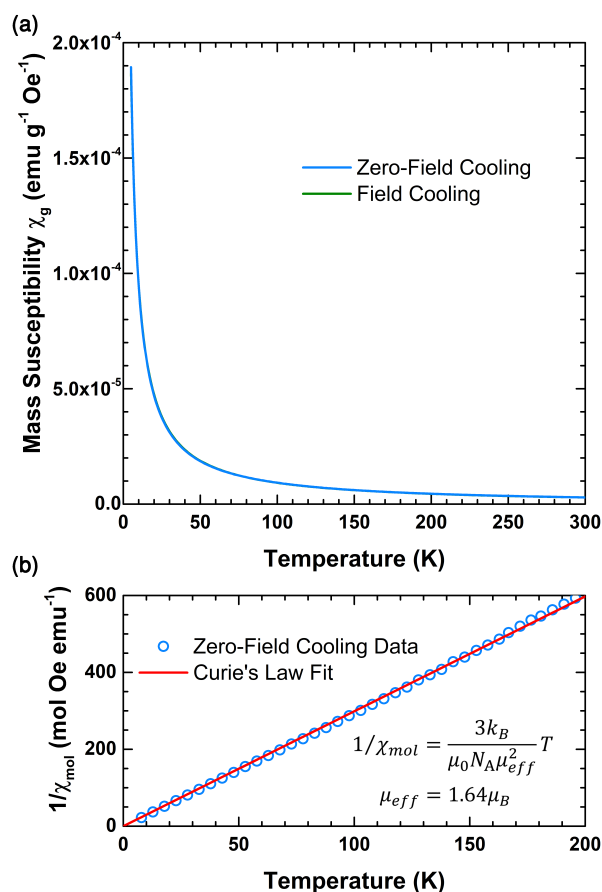


Fig. 8 (a) Temperature dependence of the magnetic susceptibility of $[\text{Cu}(\text{en-N})(\text{en-N,N}')_2](\text{NO}_3)_2$ crystals under zero-field cooling and field cooling, which overlap each other. (b) Fitting of the zero-field cooling data to Curie's Law over the temperature range of 5–200 K. This crystal is a paramagnet, with an estimate of 1.64 μ_B effective moment per Cu(II).

magnet. We speculate that the formation of this complex crystal occurs when the effective en concentration is too high to permit $[\text{Cu}(\text{en})_2]^{2+}$ crystal formation but too low to stabilize octahedral $[\text{Cu}(\text{en})_3]^{2+}$ in solution.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgments

This work was supported by the US Department of Energy, Basic Energy Sciences (grant No. DE-SC0013897) for Early Career Research. Single crystal X-ray diffraction was performed in the Georgy L. Clark X-Ray Facility and 3M Materials Laboratory, University of Illinois at Urbana-Champaign. We thank Danielle Gray and Toby Woods for their assistance in collecting diffraction data. Elemental analysis was performed by the Microanalysis Laboratory staff at University of Illinois at Urbana-Champaign. All other characterization was performed in the Materials Research Laboratory Central Facilities, University of Illinois at Urbana-Champaign.

References

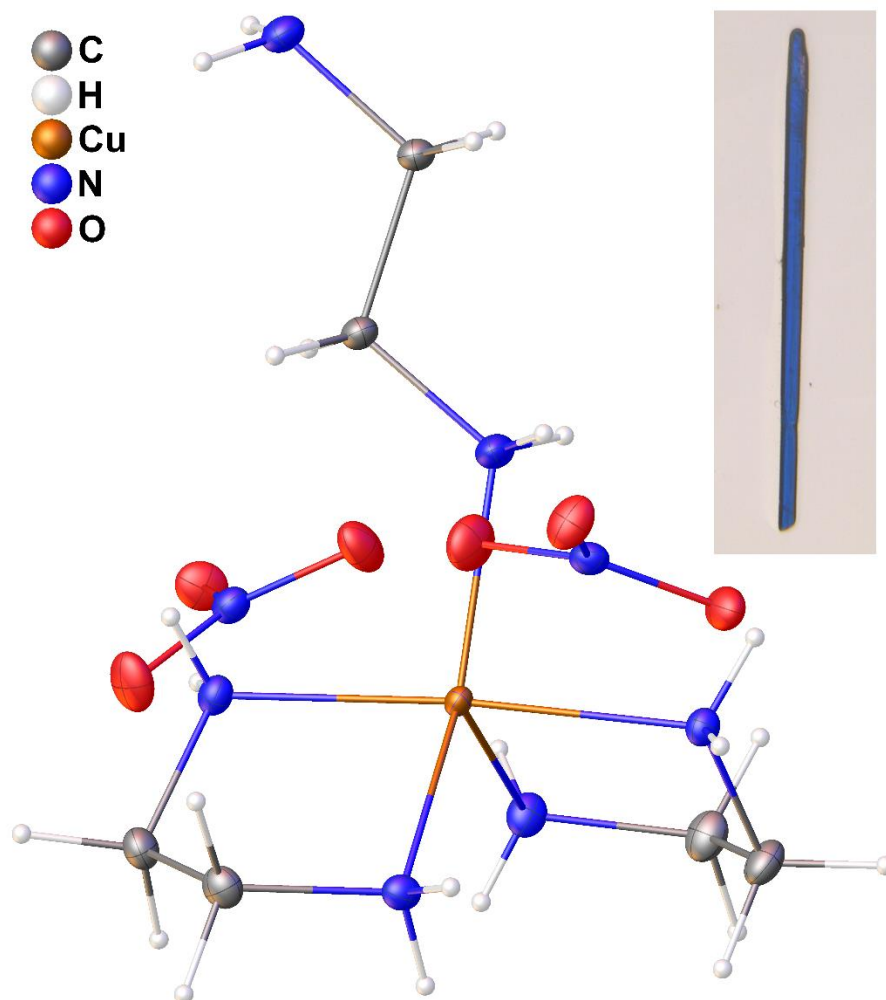
- G. Wilkinson, R. D. Gillard and J. A. McCleverty, *Comprehensive coordination chemistry: the synthesis, reactions, properties & applications of coordination compounds*, Oxford, England; New York: Pergamon Press, 1st edn., 1987.
- W. Korfmacher, T. Getek, E. Hansen and C. Cerniglia, *Anal. Biochem.*, 1990, **185**, 136–142.
- F. Crea, A. Galassi, J. C. Kaski, G. Pupita, H. E. Tamimi, G. Davies and A. Maseri, *Lancet*, 1989, **333**, 683–686.
- S. Hermansky, R. Yang, R. Garman and H. Leung, *Food Chem. Toxicol.*, 1999, **37**, 765–776.
- D. F. Clemens, B. M. Whitehurst and G. B. Whitehurst, *Fertil. Res.*, 1990, **25**, 127–131.
- M. C. Delpech and G. S. Miranda, *Cent. Eur. J. Eng.*, 2012, **2**, 231–238.
- J. Wang and G. N. Ramaswamy, *Text. Res. J.*, 2003, **73**, 339–344.
- G. R. Maxwell, in *Ethylenediamine and Chelating Agents*, Springer US, Boston, MA, 2004, pp. 325–331.
- I. Han, Z. Jiang, C. dela Cruz, H. Zhang, H. Sheng, A. Bhutani, D. J. Miller and D. P. Shoemaker, *J. Solid State Chem.*, 2018, **260**, 1–6.
- M. Nath, A. Choudhury, A. Kundu and C. Rao, *Adv. Mater.*, 2003, **15**, 2098–2101.
- W. Wang, Y. Geng, P. Yan, F. Liu, Y. Xie and Y. Qian, *J. Am. Chem. Soc.*, 1999, **121**, 4062–4063.
- M. D. Alexander and C. A. Spillert, *Inorg. Chem.*, 1970, **9**, 2344–2346.
- R. F. Childers, K. G. Vander Zyl, D. A. House, R. G. Hughes and C. S. Garner, *Inorg. Chem.*, 1968, **7**, 749–754.
- D. H. Busch, K. Swaminathan and D. W. Cooke, *Inorg. Chem.*, 1962, **1**, 260–267.
- D. F. Martin and M. L. Tobe, *J. Chem. Soc.*, 1962, 1388–1396.
- S. C. Pyke and R. G. Linck, *Inorg. Chem.*, 1971, **10**, 2445–2449.
- R. L. Fanshawe, A. Mobinikhaledi, C. R. Clark and A. G. Blackman, *Inorg. Chim. Acta*, 2000, **307**, 27–32.
- O. Z. Yeşilel, H. Ölmez and C. Arici, *Polyhedron*, 2007, **26**, 3669–3674.
- D. A. House and P. J. Steel, *Inorg. Chim. Acta*, 1999, **288**, 53–56.
- P. O. Brown, G. D. Enright and J. A. Ripmeester, *Chem. Asian J.*, 2006, **1**, 529–535.
- M. Duggan, N. Ray, B. Hathaway, G. Tomlinson, P. Brint and K. Pelin, *J. Chem. Soc., Dalton Trans.*, 1980, **0**, 1342–1348.
- O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.
- G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2015, **71**, 3–8.
- G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3–8.
- M. A. Halcrow, *Chem. Soc. Rev.*, 2013, **42**, 1784–1795.
- B. J. Hathaway, *Inorganic Chemistry*, Berlin, Heidelberg, 1973, pp. 49–67.
- A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349–1356.
- S. F. Palopoli, S. J. Geib, A. L. Rheingold and T. B. Brill, *Inorg. Chem.*, 1988, **27**, 2963–2971.
- H. Ogino and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 1836–1841.
- M. Alexander and H. G. Kilcrease, *J. Inorg. Nucl. Chem.*, 1973, **35**, 1583–1590.
- Y. Komiyama and E. C. Lingafelter, *Acta Crystallogr.*, 1964, **17**, 1145–1148.
- K. R. Maxcy and M. M. Turnbull, *Acta Crystallogr., Sect. C: Struct. Chem.*, 1999, **55**, 1986–1988.
- B. W. Brown and E. C. Lingafelter, *Acta Crystallogr.*, 1964, **17**, 254–259.
- D. S. Brown, J. D. Lee and B. G. A. Melsom, *Acta Crystallogr., Sect. B: Struct. Sci. Cryst. Eng. Mat.*, 1968, **24**, 730–734.
- T. D. Keene, M. B. Hursthouse and D. J. Price, *CrystEngComm*, 2012, **14**, 116–123.
- D. N. K. Pham, M. Roy, J. A. Golen and D. R. Manke, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2017, **73**, 442–446.
- S.-E. H. Etaiw, S. N. Abdou and A. S. Badr El-din, *J. Inorg. Organomet. Polym. Mater.*, 2015, **25**, 1394–1406.
- M.-T. Li, C.-G. Wang, Y. Wu and X.-C. Fu, *Acta Crystallogr., Sect. E: Crystallogr. Commun.*, 2005, **61**, m1660–m1661.
- T. Akitsu and Y. Einaga, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 763–764.
- R. J. Williams, A. C. Larson and D. T. Cromer, *Acta Crystallogr., Sect. B: Struct. Sci. Cryst. Eng. Mat.*, 1972, **28**, 858–864.
- T. M. Anderson, M. A. Rodriguez, T. A. Stewart, J. N. Bixler, W. Xu, J. B. Parise and M. Nyman, *Eur. J. Inorg. Chem.*, 2008, **2008**, 3286–3294.
- M. Melník, M. Kabešová, M. Dunaj-Jurčo and C. E. Holloway, *J. Coord. Chem.*, 1997, **41**, 35–182.
- J. Bjerrum, C. J. Ballhausen, C. K. Jørgensen and N. A. Sørensen, *Acta Chem. Scand.*, 1954, **8**, 1275–1289.

- 44 S. Smeets, P. Parois, H.-B. Bürgi and M. Lutz, *Acta Crystallogr., Sect. B: Struct. Sci. Cryst. Eng. Mat.*, 2011, **67**, 53–62.
- 45 K. Krishnan and R. A. Plane, *Inorg. Chem.*, 1966, **5**, 852–857.
- 46 V. S. Sastri, J.-C. Bünzli, V. R. Rao, G. Rayudu and J. Perumareddi, *Modern Aspects of Rare Earths and Their Complexes*, Elsevier, 2003.
- 47 X. Wang and D.-S. Yang, *J. Phys. Chem. A*, 2006, **110**, 7568–7576.
- 48 P. M. Castro and P. W. Jagodzinski, *Spectroc. Acta, Pt. A: Molec. Spectr.*, 1991, **47**, 1707–1720.
- 49 Z. Gabelica, *Spectroc. Acta, Pt. A: Molec. Spectr.*, 1976, **32**, 327–336.
- 50 Z. Gabelica, *Spectroc. Acta, Pt. A: Molec. Spectr.*, 1976, **32**, 337–344.
- 51 K. Nakamoto, in *Applications in Coordination Chemistry*, John Wiley & Sons, Ltd, 2008, ch. 1, pp. 1–273.
- 52 J. P. Donoso, C. J. Magon, J. F. Lima, O. R. Nascimento, E. Benavente, M. Moreno and G. Gonzalez, *J. Phys. Chem. C*, 2013, **117**, 24042–24055.
- 53 F. Velghe, R. A. Schoonheydt, J. B. Uytterhoeven, P. Peigneur and J. H. Lunsford, *J. Phys. Chem.*, 1977, **81**, 1187–1194.
- 54 A. R. Rossi and R. Hoffmann, *Inorg. Chem.*, 1975, **14**, 365–374.
- 55 A. A. G. Tomlinson and B. J. Hathaway, *J. Chem. Soc. A*, 1968, 1905–1909.
- 56 I. M. Procter, B. J. Hathaway and P. Nicholls, *J. Chem. Soc. A*, 1968, 1678–1684.

A unique copper coordination structure with both mono- and bi-dentate ethylenediamine ligands

Table of Content

Jai Sharma, Zhelong Jiang, Ankita Bhutani, Piush Behera and Daniel P. Shoemaker *



A new crystal structure achieving penta-coordination using exclusively ethylenediamine ligands is discovered for the first time.