Electronic Supplementary Material (ESI) for CrystEngComm.

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

Supplementary Information

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Table S1 Crystal data and refinement details for (ethylenediamine-N)-bis(ethylenediamine-N,N')-copper(II) bis(nitrate)

empirical formula	$C_6H_{24}CuN_8O_6$
formula weight	367.87
temperature (K)	99.96
crystal system	monoclinic
space group	$P2_1/c$
a (Å)	12.8262(5)
b (Å)	9.7712(4)
c (Å)	11.9065(5)
β (°)	94.8220(10)
volume (Å^3)	1486.93(10)
Z	4
ρ_{calc} (g/cm^3)	1.643
μ (mm^{-1})	1.511
F(000)	772.0
crystal size (mm^3)	0.319 × 0.113 × 0.093
radiation	Mo Kα (λ = 0.71073 Å)
2Θ range for data collection (°)	5.248 to 56.634
index ranges	-17≤ h ≤17, -13≤ k ≤13, -15≤ l ≤15
reflection collected	35107
independent reflections	3700 [R_{int}=0.0362, R_{sigma}=0.0164]
absorption correction	multi-scan (*SADABS*-2016/2; Bruker, 2016)
max. and min. transmission	0.7457 and 0.6107
data/restraints/parameters	3700/0/239
goodness-of-fit on F^2	1.092
final R indexes [I≥2σ(I)]	R_1=0.0204, wR_2=0.0477
final R indexes (all data)	R_1=0.0235, wR_2=0.0489
largest diff. peak/hole (e Å^3)	0.47/-0.34
omitted reflection	(202) (partially obscured by beamstop)
H-atom treatment	CH_2 hydrogen atoms constrained with idealized riding contributors: C–H = 0.99 Å, U_{iso}(H) = 1.2 U_{eq}(C)

Table S2 Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $[Cu(en\text{-}N)(en\text{-}N,N')_2](NO_3)_2$. The crystal has space group $P2_1/c$, with a = 12.8262(5) Å, b = 9.7712(4) Å, c = 11.9065(5) Å, and β = 94.8220(10) °. The data was collected at 99.96 K. Hydrogen atom coordinates are provided in Table S3.

Atom	x	y	z	**U(eq)**
Cu(1)	0.77022(2)	0.07870(2)	0.25688(2)	0.00713(6)
N(1)	0.73723(9)	-0.01800(12)	0.08986(9)	0.0122(2)
N(2)	0.92029(8)	0.03499(11)	0.22635(9)	0.0093(2)
N(3)	0.76670(9)	-0.07708(11)	0.37197(9)	0.0101(2)
N(4)	0.61950(8)	0.10589(11)	0.28731(9)	0.0105(2)
N(5)	0.80017(9)	0.28290(11)	0.22735(11)	0.0146(2)
N(6)	0.70314(9)	0.64783(11)	0.26478(10)	0.0134(2)
C(1)	0.83916(10)	-0.05158(14)	0.04763(11)	0.0146(2)
C(2)	0.91836(10)	-0.08133(13)	0.14685(11)	0.0139(2)
C(3)	0.67263(10)	-0.05732(13)	0.43371(10)	0.0122(2)
C(4)	0.58395(10)	-0.01559(13)	0.34804(11)	0.0122(2)
C(5)	0.72527(9)	0.39334(12)	0.24597(10)	0.0105(2)
C(6)	0.77382(9)	0.53596(12)	0.24033(10)	0.0101(2)
O(1)	1.03807(7)	0.12595(9)	0.44802(8)	0.01368(18)
O(2)	1.00958(7)	0.20804(10)	0.61215(7)	0.01544(19)
O(3)	0.88349(7)	0.20377(10)	0.47803(8)	0.0186(2)
N(7)	0.97700(8)	0.17867(10)	0.51220(9)	0.0102(2)
O(4)	0.60586(7)	0.22205(10)	-0.00091(8)	0.0172(2)
O(5)	0.47413(7)	0.12980(11)	0.07470(8)	0.0178(2)
O(6)	0.45479(7)	0.20662(10)	-0.09722(8)	0.01535(19)
N(8)	0.51145(8)	0.18576(10)	-0.00768(9)	0.0104(2)

Table S3 Hydrogen atom coordinates and equivalent isotropic displacement parameters (Å^2) for [Cu(en-N)(en-N,N')$_2$](NO$_3$)$_2$ with space group P2$_1$/c, a = 12.8262(5) Å, b = 9.7712(4) Å, c = 11.9065(5) Å, and β = 94.8220(10) °. CH$_2$ hydrogens were constrained while NH$_2$ hydrogens were freely refined.

Atom	*x*	*y*	*z*	U(eq)
H(1A)	0.7041(15)	0.0400(20)	0.0455(16)	0.027(5)
H(1B)	0.7011(15)	-0.0860(20)	0.0923(16)	0.026(5)
H(2A)	0.9493(14)	0.1051(19)	0.1968(15)	0.023(5)
H(2B)	0.9565(13)	0.0160(17)	0.2877(15)	0.016(4)
H(3A)	0.7611(13)	-0.1558(18)	0.3366(14)	0.017(4)
H(3B)	0.8189(15)	-0.0784(17)	0.4158(15)	0.019(4)
H(4A)	0.5821(14)	0.1197(19)	0.2243(16)	0.025(5)
H(4B)	0.6119(13)	0.1741(18)	0.3276(15)	0.020(4)
H(5A)	0.8201(15)	0.2910(20)	0.1613(17)	0.031(5)
H(5B)	0.8536(17)	0.2920(20)	0.2729(18)	0.035(5)
H(6A)	0.6575(15)	0.6594(19)	0.2078(16)	0.026(5)
H(6B)	0.6708(14)	0.6311(18)	0.3207(16)	0.020(4)
H(1C)	0.863583	0.026226	0.003481	0.018
H(1D)	0.831715	-0.132555	-0.002372	0.018
H(2C)	0.898778	-0.166268	0.185232	0.017
H(2D)	0.988626	-0.094449	0.119925	0.017
H(3C)	0.68532	0.014896	0.491569	0.015
H(3D)	0.654808	-0.143296	0.471702	0.015
H(4C)	0.566752	-0.091363	0.294463	0.015
H(4D)	0.520658	0.006929	0.386528	0.015
H(5C)	0.698334	0.380821	0.320808	0.013
H(5D)	0.665201	0.386599	0.188319	0.013
H(6C)	0.836501	0.540213	0.294738	0.012
H(6D)	0.797217	0.549815	0.164008	0.012

Table S4 Anisotropic displacement parameters (Å^2) for [Cu(en-N)(en-N,N')$_2$](NO$_3$)$_2$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	0.00669(8)	0.00657(8)	0.00830(8)	0.00022(5)	0.00159(5)	0.00123(5)
N(1)	0.0106(5)	0.0143(5)	0.0113(5)	-0.0018(4)	-0.0008(4)	0.0007(4)
N(2)	0.0082(5)	0.0104(5)	0.0093(5)	-0.0006(4)	0.0003(4)	0.0009(4)
N(3)	0.0096(5)	0.0093(5)	0.0114(5)	0.0007(4)	-0.0005(4)	0.0000(4)
N(4)	0.0100(5)	0.0112(5)	0.0103(5)	0.0001(4)	0.0018(4)	0.0018(4)
N(5)	0.0125(5)	0.0084(5)	0.0237(6)	0.0003(4)	0.0052(5)	0.0011(4)
N(6)	0.0137(5)	0.0093(5)	0.0175(6)	-0.0010(4)	0.0022(5)	0.0019(4)
C(1)	0.0149(6)	0.0181(6)	0.0109(6)	-0.0030(5)	0.0013(5)	0.0027(5)
C(2)	0.0125(6)	0.0141(6)	0.0153(6)	-0.0045(5)	0.0013(5)	0.0035(5)
C(3)	0.0129(6)	0.0134(6)	0.0106(6)	0.0016(4)	0.0022(4)	-0.0008(5)
C(4)	0.0097(6)	0.0132(6)	0.0138(6)	0.0002(5)	0.0024(4)	-0.0014(4)
C(5)	0.0110(5)	0.0077(5)	000131(6)	0.0003(4)	0.0025(4)	0.0010(4)
C(6)	0.0105(5)	0.0073(5)	0.0127(6)	-0.0001(4)	0.0017(4)	0.0002(4)
O(1)	0.0159(4)	0.0137(4)	0.0121(4)	-0.0022(3)	0.0055(3)	-0.0001(3)
O(2)	0.0169(5)	0.0199(5)	0.0092(4)	-0.0029(3)	-0.0009(3)	0.0047(4)
O(3)	0.0115(4)	0.0221(5)	0.0211(5)	-0.0009(4)	-0.0040(4)	0.0034(4)
N(7)	0.0121(5)	0.0079(4)	0.0108(5)	0.0015(4)	0.0014(4)	-0.0002(4)
O(4)	0.0104(4)	0.0195(5)	0.0213(5)	0.0063(4)	-0.0014(4)	-0.0027(4)
O(5)	0.0159(5)	0.0264(5)	0.0115(4)	0.0067(4)	0.0039(4)	-0.0003(4)
O(6)	0.0161(5)	0.0176(4)	0.0114(4)	0.0030(3)	-0.0043(3)	0.0001(4)
N(8)	0.0109(5)	0.0094(5)	0.0109(5)	0.0002(4)	0.0011(4)	0.0017(4)

Table S5 Bond lengths for [Cu(en-N)(en-N,N')$_2$](NO$_3$)$_2$.

Atom	Atom	Length (Å)
Cu(1)	N(1)	2.2102(11)
Cu(1)	N(2)	2.0340(10)
Cu(1)	N(3)	2.0511(10)
Cu(1)	N(4)	2.0142(11)
Cu(1)	N(5)	2.0676(11)
N(1)	C(1)	1.4765(17)
N(2)	C(2)	1.4780(16)
N(3)	C(3)	1.4773(16)
N(4)	C(4)	1.4816(16)
N(5)	C(5)	1.4739(16)
N(6)	C(6)	1.4649(16)
C(1)	C(2)	1.5199(17)
C(3)	C(4)	1.5184(17)
C(5)	C(6)	1.5301(16)
O(1)	N(7)	1.2504(14)
O(2)	N(7)	1.2607(14)
O(3)	N(7)	1.2579(14)
O(4)	N(8)	1.2579(14)
O(5)	N(8)	1.2527(14)
O(6)	N(8)	1.2554(14)

Table S6 Bond angles for [Cu(en-N)(en-N,N')$_2$](NO$_3$)$_2$.

Atom	Atom	Atom	Angle (°)
N(2)	Cu(1)	N(1)	82.06(4)
N(2)	Cu(1)	N(3)	92.17(4)
N(2)	Cu(1)	N(5)	88.86(4)
N(3)	Cu(1)	N(1)	105.70(4)
N(3)	Cu(1)	N(5)	147.63(5)
N(4)	Cu(1)	N(1)	95.98(4)
N(4)	Cu(1)	N(2)	175.46(4)
N(4)	Cu(1)	N(3)	84.40(4)
N(4)	Cu(1)	N(5)	95.63(4)
N(5)	Cu(1)	N(1)	106.49(5)
C(1)	N(1)	Cu(1)	107.06(8)
C(2)	N(2)	Cu(1)	108.10(7)
C(3)	N(3)	Cu(1)	107.47(7)
C(4)	N(4)	Cu(1)	108.75(8)
C(5)	N(5)	Cu(1)	123.25(8)
N(1)	C(1)	C(2)	109.32(10)
N(2)	C(2)	C(1)	108.96(10)
N(3)	C(3)	C(4)	107.32(10)
N(4)	C(4)	C(3)	107.40(10)
N(5)	C(5)	C(6)	112.79(10)
N(6)	C(6)	C(5)	114.20(10)
O(1)	N(7)	O(2)	119.72(10)
O(1)	N(7)	O(3)	120.79(10)
O(3)	N(7)	O(2)	119.49(10)
O(5)	N(8)	O(4)	120.13(10)
O(5)	N(8)	O(6)	120.26(10)
O(6)	N(8)	O(4)	119.61(10)

Table S7 Torsion angles for $[Cu(en\text{-}N)(en\text{-}N,N')_2](NO_3)_2$.

A	B	C	D	Angle (°)
N(1)	C(1)	C(2)	N(2)	-53.67(14)
N(3)	C(3)	C(4)	N(4)	-54.81(13)
N(5)	C(5)	C(6)	N(6)	-176.73(10)
Cu(1)	N(1)	C(1)	C(2)	30.23(12)
Cu(1)	N(2)	C(2)	C(1)	49.58(11)
Cu(1)	N(3)	C(3)	C(4)	41.67(11)
Cu(1)	N(4)	C(4)	C(3)	40.52(11)
Cu(1)	N(5)	C(5)	C(6)	168.70(8)

Table S8 Hydrogen bonds for $[Cu(en\text{-}N)(en\text{-}N,N')_2](NO_3)_2$.

D	H	A	d(D–H) (Å)	d(H–A) (Å)	d(D–A) (Å)	D–H–A (°)
N(1)	H(1A)	O(4)	0.86(2)	2.22(2)	3.0336(15)	156.9(17)
N(1)	H(1B)	O(6)^{i}	0.82(2)	2.32(2)	3.0833(15)	155.2(18)
N(2)	H(2A)	O(2)^{ii}	0.867(19)	2.254(19)	3.1188(14)	174.6(17)
N(2)	H(2B)	O(1)	0.852(18)	2.358(17)	3.0607(14)	140.1(15)
N(2)	H(2B)	O(2)^{iii}	0.852(18)	2.514(17)	3.1392(14)	131.0(14)
N(3)	H(3A)	N(6)^{iv}	0.877(18)	2.204(18)	3.0567(15)	164.0(15)
N(3)	H(3B)	O(1)^{iii}	0.814(19)	2.389(19)	3.1921(14)	169.0(16)
N(3)	H(3B)	O(2)^{iii}	0.814(19)	2.584(18)	3.1331(14)	126.1(15)
N(4)	H(4A)	O(5)	0.866(19)	2.165(19)	3.0242(14)	171.5(17)
N(4)	H(4B)	O(4)^{v}	0.831(18)	2.288(18)	3.0478(15)	152.2(16)
N(4)	H(4B)	O(6)^{v}	0.831(18)	2.555(18)	3.1934(14)	134.6(15)
N(5)	H(5A)	O(2)^{ii}	0.85(2)	2.55(2)	3.1181(15)	125.4(16)
N(5)	H(5A)	O(3)^{ii}	0.85(2)	2.39(2)	3.2411(16)	175.0(18)
N(5)	H(5B)	O(3)	0.84(2)	2.59(2)	3.1800(16)	128.3(17)
N(6)	H(6A)	O(6)^{vi}	0.866(19)	2.281(19)	3.0703(15)	151.6(17)
N(6)	H(6B)	O(5)^{vii}	0.830(19)	2.323(19)	3.0958(15)	155.2(16)
C(2)	H(2C)	O(2)^{iii}	0.99	2.63	3.1899(16)	116.3
C(3)	H(3D)	O(6)^{viii}	0.99	2.59	3.5095(16)	154.3
C(4)	H(4C)	O(6)^{i}	0.99	2.60	3.5214(16)	155.2

Symmetry codes: (i) 1-x,-y,-z; (ii) x,1/2-y,-1/2+z; (iii) 2-x,-y,1-z; (iv) x,-1+y,z; (v) x,1/2-y,1/2+z; (vi) 1-x,1-y,-z; (vii) 1-x,1/2+y,1/2-z; (viii) 1-x,-1/2+y,1/2-z.

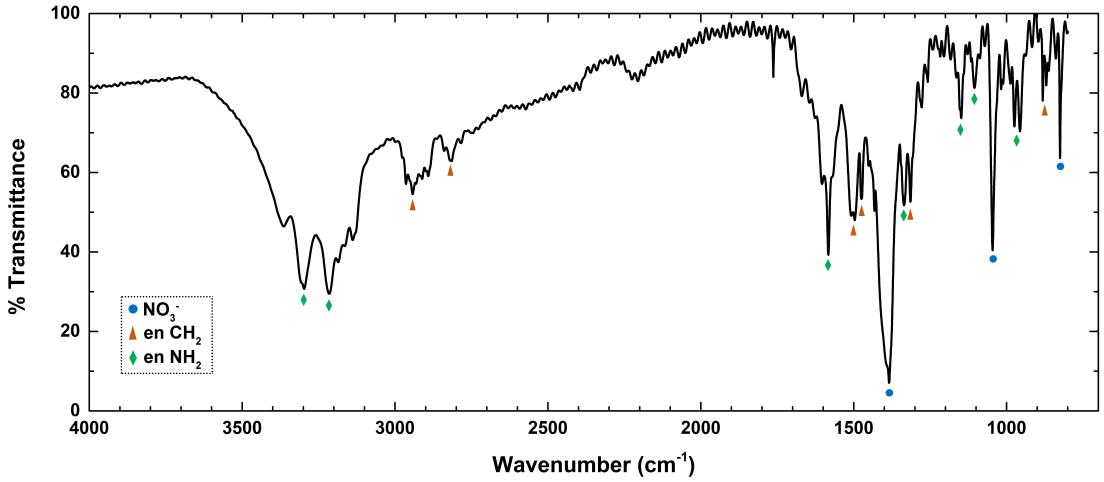

Fig. S1 FTIR spectrum of $[Cu(en\text{-}N)(en\text{-}N,N')_2](NO_3)_2$ crystals. It shows absorption peaks arising from NO_3^-, and the CH_2 and NH_2 groups in en. The background wiggling is due to interference effects from the KBr pellet method.

Table S9 FTIR group assignment for $[Cu(en\text{-}N)(en\text{-}N,N')_2](NO_3)_2$ in Fig. S1.

Wavenumber (cm^{-1})	Intensity [a]	Group Assignment
825	m	NO_3^- scissor [1]
882	w	CH_2 rock [2]
957	m	NH_2 twist [2]
975	m	NH_2 twist [2]
1046	s	NO_3^- symmetric stretch [1], C-N stretch [2]
1105	w	NH_2 twist [2]
1148	m	NH_2 wag [2]
1314	m	CH_2 twist [2,3]
1335	m	NH_2 wag [2]
1385	s	NO_3^- antisymmetric stretch [1]
1396	sh	NH_2 wag [3,4] / CH_2 wag [2]
1474	m	CH_2 scissor [2]
1497	m	CH_2 scissor [2]
1583	s	NH_2 scissor [2,4]
2815 (2777 - 2848)	w, br	CH_2 stretch [2]
2942 (2878 - 2981)	w, br	CH_2 stretch [2]
3216 & 3297 (3110 - 3457)	m, br	NH_2 stretch [2,4]

[a] s = strong; m = medium; w = weak; sh = shoulder; br = broad.

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