Three new binuclear copper(II) complexes with isonicotinic acid *N*-oxide: syntheses, crystal structures and properties

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THREE NEW BINUCLEAR COPPER(II) COMPLEXES WITH ISONICOTINIC ACID *N*-OXIDE: SYNTHESES, CRYSTAL STRUCTURES AND PROPERTIES

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Three new copper(II) complexes with isonicotinic acid *N*-oxide (HL) and 1,10-phenanthroline (phen) as ligands, $[Cu(L)(phen)(H_2O)]_2(NO_3)_2 \cdot 2H_2O$ (**1**), $[Cu(L)(phen)(H_2O)]_2(ClO_4)_2 \cdot 2H_2O$ (**2**), and $[Cu(L)(phen)Br]_2$-$[Cu(L)(phen)(H_2O)]_2Br_2 \cdot 6H_2O$ (**3**) have been synthesized and structurally characterized. The structures of all three complexes feature a Cu_2 dimer formed by two Cu(II) ions interconnected by two bridging ligands. Each copper(II) ion has a distorted square pyramidal coordination geometry with elongated axial coordination by an aqua ligand or halogen anion. The isonicotinic acid *N*-oxide anion is bidentate, being coordinated to two Cu(II) ions through its *N*-O oxygen and one of its carboxylate oxygen atoms. Magnetic susceptibility measurements show a Curie–Weiss paramagnetic behavior characteristic of one unpaired electron for a copper(II) ion for all three complexes.

Keywords: Isonicotinic acid *N*-oxide; Copper(II); Crystal structure; Paramagnetic complexes; 1,10-phenanthroline; Binuclear complexes

INTRODUCTION

Magnetic centers are capable of interacting through extended bridging ligands, even if these centers are relatively far away from each other [1]. One such ligand is the terephthalato dianion and its analogues with two chelating carboxyl groups about 7 Å apart. Novel terephthalato-bridged d^9–d^9 magnetic systems have attracted much attention, focusing on the magnetic exchange mechanisms [2–4]. These studies have demonstrated the importance of both the geometry of magnetic centers and the coordination mode of bridging ligands in tuning magnetic exchange interactions. In an effort to explore new copper(II) compounds with potential magnetic properties,

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we use isonicotinic acid *N*-oxide, a heterocyclic aromatic ligand, as a metal linker. 1,10-phenanthroline was also used as a terminal ligand to trap the dinuclear copper(II) centers. Although several copper(II) complexes with isonicotinic acid *N*-oxide have been reported [5,6], to the best of our knowledge, no copper(II) complex has been reported with coordination of the *N*-oxide group with copper(II). A similar coordination mode was observed in the isomeric picolinic acid *N*-oxide complex with Cu [7] and isonicotinic acid *N*-oxide complexes with Sn [8] and Cd [9]. Herein we report the syntheses, crystal structures, magnetic properties and EPR studies of three dinuclear copper(II) complexes in which the metal centers are bridged by the isonicotinic acid *N*-oxide ligands, namely, $[Cu(L)(phen)(H_2O)]_2(NO_3)_2 \cdot 2H_2O$ (HL = isonicotinic acid *N*-oxide) (**1**), $[Cu(L)(phen)(H_2O)]_2(ClO_4)_2 \cdot 2H_2O$ (**2**) and $[Cu(L)(phen)Br]_2[Cu(L)(phen)(H_2O)]_2 \ Br_2 \cdot 6H_2O$ (**3**).

EXPERIMENTAL

Materials and Methods

Copper(II) nitrate trihydrate, copper(II) perchlorate hexahydrate, copper bromide, isonicotinic acid *N*-oxide (HL) and 1,10-phenanthroline were purchased from commercial sources and used without further purification. All solvents were of analytical grade and used as received. The FTIR spectra were recorded on a Nicolet Magna 750 FTIR spectrometer using KBr pellets (4000–400 cm^{-1}). Magnetic susceptibility measurements on polycrystalline samples were performed with a Quantum Design SQUID magnetometer at a field of 1 T over the range 6–300 K. The raw data were corrected for the susceptibility of the container. Isotropic X-band EPR spectra of the complexes were recorded on a Bruker ER-420 spectrometer at room temperature (293 K) with a frequency modulation of 100 kHz. The elemental analyses were performed using a German Elementary Vario EL III instrument.

Synthesis of $[Cu(L)(phen)(H_2O)]_2(NO_3)_2 \cdot 2H_2O$ (1)

Small dark-green brick-shaped crystals of **1** were obtained in 65% yield by the solvothermal reaction of $[Cu(NO_3)_2] \cdot 3H_2O$, HL and 1,10-phenanthroline in a molar ratio of 1:1:1 in 50% aqueous ethanol at 180°C for one day. Anal. Calcd. for $C_{36}H_{32}Cu_2N_8O_{16}$(%): C, 45.0; H, 3.4; N, 11.7. Found: C, 44.6; H, 3.0; N, 11.5. IR (KBr, cm^{-1}): υ(OH) 3000–3600 w; υ_{as}(C=O)1628, υ_s(C=O)1363; υ(NO$_3^-$)1380, 835; υ(N–O) 1205, δ(N–O) 852.

Synthesis of $[Cu(L)(phen)(H_2O)]_2(ClO_4)_2 \cdot 2H_2O$ (2)

A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.185 g, 0.5 mmol), HL (0.034 g, 0.25 mmol) and phen (0.049 g, 0.25 mmol) in the mixed solvent methanol (10 cm^3) and MeCN (10 cm^3) was continuously stirred at room temperature for 8 h. The green precipitates were filtered off and the filtrate was allowed to evaporate slowly at room temperature in an open vessel. Prismatic green crystals of **2** were obtained after a few days. Anal. Calcd. for $C_{36}H_{32}Cl_2Cu_2N_6O_{18}$(%): Cu, 12.3; C, 41.8; N, 8.1; Found: Cu, 12.8; C, 42.6; N, 8.0.

IR (KBr, cm^{-1}): υ(OH) 3000–3600 w; υ_{as}(C=O)1626, υ_s(C=O)1365; υ(ClO$_4^-$)1090, 627; υ(N–O) 1205, δ(N–O) 852.

Synthesis of [Cu(L)(phen)Br]$_2$[Cu(L)(phen)(H$_2$O)]$_2$Br$_2 \cdot$ 6H$_2$O (3)

Prismatic green crystals of **3** were isolated in 60% yield by solvothermal reactions of CuBr, HL and 1,10-phen in a molar ratio of 1:1:1 in 50% aqueous ethanol at 180°C for one day. Anal. Calcd. for C$_{72}$H$_{64}$Br$_4$Cu$_4$N$_{12}$O$_{20}$(%): C, 43.4; H, 3.2; Found: C, 43.6; H, 2.5. IR (KBr, cm^{-1}): υ(OH) 3000–3600 w; υ_{as}(C=O)1626, υ_s(C=O)1363; υ(N–O) 1203, δ(N–O) 856.

Single-crystal Structure Determination

Single crystals with dimensions of $0.86 \times 0.12 \times 0.06$, $0.34 \times 0.24 \times 0.16$ and $0.66 \times 0.30 \times 0.26$ mm^3, respectively for **1**, **2** and **3**, were mounted on a Siemens Smart CCD diffractometer equipped with graphite-monochromated MoKα radiation ($\lambda =$ 0.71073 Å). Intensity data were collected by the narrow-frame method with 0.3° per frame in ω at 293 K. A total of 3326 (**1**), 3521 (**2**) and 6547 (**3**) independent reflections were collected, respectively, in which 2702 (**1**), 2937 (**2**) and 5087 (**3**) reflections were considered to be observed ($I > 2.0\sigma(I)$). Absorption corrections were performed by the SADABS program [10]. All structures were solved by direct methods, and refined by full-matrix least-squares fitting on F^2 by SHEXLS 97 [11]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at geometrically calculated positions. Detailed crystallographic data for these three compounds are listed in Table I, final atomic positional parameters for **1**, **2** and **3** are presented in

TABLE I Summary of cell parameters and data collection for salts **1**, **2** and **3**

Salt	**1**	**2**	**3**
Empirical formula	C$_{36}$H$_{32}$Cu$_2$N$_8$O$_{16}$	C$_{36}$H$_{32}$Cl$_2$Cu$_2$N$_6$O$_{18}$	C$_{72}$H$_{64}$Br$_4$Cu$_4$N$_{12}$O$_{20}$
Mr	959.78	1034.66	1991.15
Space group	P-1	P-1	P-1
a(Å)	8.7125(3)	8.9476(7)	8.4294(2)
b(Å)	9.1209(2)	9.7948(8)	14.9997(2)
c(Å)	12.7610(3)	12.3146(10)	16.3281(4)
α(°)	85.701(2)	82.1630(10)	104.9530(10)
β(°)	83.420(2)	85.0030(10)	103.9250(10)
γ(°)	71.445(2)	71.3640(10)	99.6040(10)
V(Å^3)	954.22(4)	1012.02(14)	1877.39(7)
Z	1	1	1
D_{calc} (g cm^{-3})	1.670	1.698	1.761
F(000)	490	526	996
μ (MoKα)(mm^{-1})	1.202	1.270	3.328
Max. and min. trans. factor	1.000–0.787	1.000–0.729	1.000–0.673
Data collected	4954	5233	9759
Unique data (R_{int})	3326(2.25%)	3521(2.29%)	6547 (2.21%)
Observed data [$I > 2\sigma(I)$]	2702	2937	5087
No. parameters refined	280	289	506
Residual extremes (e Å^{-3})	0.628, −0.450	0.597, −0.409	0.576, −0.511
Goodness of fit	1.083	1.097	1.116
R_1, wR_2	0.0592, 0.1512	0.0596, 0.1454	0.0447, 0.0986

R$_1 = \sum(\||F_0|-|F_c\||)/\sum|F_0|$; $wR_2 = [\sum w(F_0-F_c)^2/\sum w(F_0)^2]^{1/2}$.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for non-hydrogen atoms in **1**

Atom	x/a	y/b	z/c	U_{eq}[a]
Cu(1)	6287(1)	6732(1)	7562(1)	46(1)
O(3)	8338(4)	6679(5)	6779(3)	55(1)
N(2)	4402(5)	6478(5)	8516(3)	43(1)
N(3)	6718(5)	7606(5)	8868(3)	45(1)
O(2)	5714(4)	5549(5)	6499(3)	61(1)
N(1)	6732(5)	5242(5)	5610(3)	50(1)
C(18)	5577(6)	7596(5)	9693(3)	41(1)
C(17)	8997(6)	3544(6)	4680(4)	47(1)
C(16)	3109(6)	6910(6)	10304(4)	47(1)
C(15)	9008(6)	4694(6)	3910(3)	42(1)
O(1)	5076(5)	9076(5)	6854(4)	74(1)
C(14)	5606(7)	8134(6)	10690(4)	51(1)
C(13)	4325(6)	6989(5)	9496(4)	41(1)
C(12)	7838(7)	3851(6)	5528(4)	53(1)
C(11)	7777(6)	6075(6)	3977(4)	51(1)
C(10)	6628(7)	6344(7)	4847(4)	58(1)
C(9)	2009(6)	5764(6)	9076(4)	53(1)
C(8)	4338(8)	8051(6)	11498(4)	59(2)
C(7)	3263(6)	5894(6)	8310(4)	48(1)
C(6)	3160(7)	7477(6)	11313(4)	59(2)
C(5)	8012(7)	8744(7)	9979(5)	58(1)
C(4)	1937(6)	6265(6)	10061(4)	53(1)
C(3)	6875(7)	8721(6)	10815(4)	58(1)
C(2)	7882(6)	8184(6)	9011(5)	55(1)
N(4)	796(7)	9985(7)	7080(5)	73(1)
O(7)	1857(8)	10337(9)	6510(6)	140(3)
O(4)	9675(5)	4522(5)	7658(3)	74(1)
C(1)	9576(6)	5500(7)	6932(4)	48(1)
O(6)	999(10)	9589(9)	7980(6)	143(3)
O(5)	−524(8)	10238(10)	6793(7)	156(3)
O(8)	−2977(6)	10441(6)	5582(4)	91(2)

[a]U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Tables II–IV, respectively. Selected bond distances and angles for **1**–**3** are given in Tables V and VI, respectively.

RESULTS AND DISCUSSION

Crystal Structures

The structures of **1**, **2** and **3** all contain $[Cu(L)(phen)(H_2O)]_2^{2+}$ with a Cu_2 dimer formed by two isonicotinic *N*-oxide ligands and two Cu(II) ions (Fig. 1). The same dimer ring has been reported in the homologous Cd(II) complex. However, such dimer rings in the cadmium(II) complex are interconnected into a 1D chain by sharing metal centers [9]. In **1**, **2** and **3**, the Cu_2 dimer rings remain isolated because of the terminal phen ligands. Each copper(II) ion has distorted square-pyramidal coordination geometry. The square plane is formed by an *N*-O oxygen of a ligand, one carboxyl oxygen of another ligand, and two nitrogen atoms from a phenanthroline ligand, the apex of the pyramid being occupied by an aqua ligand (Fig. 1). In addition to $([Cu(L)(phen)(H_2O)]_2^{2+}$, **3** also contains a neutral $[Cu(L)(phen)Br]_2$ dimeric ring, in which the bromine anion occupies

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for non-hydrogen atoms in **2**

Atom	x/a	y/b	z/c	U_{eq} [a]
Cu(1)	6363(1)	6707(1)	7457(1)	46(1)
Cl(1)	10869(2)	9950(2)	7133(1)	60(1)
O(3)	8350(4)	6675(4)	6680(3)	53(1)
N(2)	4527(5)	6459(4)	8418(3)	43(1)
O(2)	5790(4)	5627(5)	6391(3)	62(1)
N(3)	6777(5)	7546(5)	8769(3)	49(1)
C(18)	5650(6)	7556(5)	9589(4)	47(1)
N(1)	6813(5)	5290(5)	5523(3)	49(1)
C(17)	3454(6)	5861(6)	8229(4)	51(1)
O(4)	9591(5)	4698(5)	7770(3)	71(1)
C(16)	4451(6)	6964(5)	9407(4)	45(1)
C(15)	3270(7)	6881(6)	10218(4)	54(1)
C(14)	10917(6)	5341(5)	6136(3)	40(1)
C(13)	9015(6)	3630(6)	4741(4)	45(1)
C(1)	9531(6)	5575(6)	6957(4)	46(1)
C(12)	7912(6)	5988(6)	3830(4)	53(1)
C(11)	6782(6)	6288(6)	4666(4)	54(1)
C(10)	5652(7)	8077(6)	10596(4)	58(1)
C(9)	2255(6)	5724(7)	8994(5)	61(2)
O(9)	6849(6)	10764(6)	5700(4)	92(2)
C(8)	7862(6)	3968(6)	5553(4)	52(1)
C(7)	2162(7)	6248(6)	9986(5)	63(2)
C(6)	3302(8)	7450(7)	11235(5)	71(2)
C(5)	6900(9)	8621(7)	10717(5)	73(2)
O(1)	5195(6)	8919(5)	6547(5)	94(2)
C(4)	4429(9)	8007(7)	11407(5)	74(2)
C(3)	7920(7)	8063(7)	8917(5)	64(2)
C(2)	8022(8)	8625(7)	9884(6)	73(2)
O(8)	11199(13)	8674(8)	6671(7)	181(4)
O(7)	11988(8)	10640(7)	6697(7)	137(3)
O(6)	9384(8)	10800(10)	6940(7)	177(4)
O(5)	11055(10)	9521(8)	8258(5)	138(3)

[a]U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

the apex of the square pyramid (Fig. 2). In both Cu_2 dimers, the phenanthroline acts as a bidentate chelating ligand.

The Cu–N distances are in the range of 1.994(4)–2.027(4) Å, and Cu–O (COO) distances range from 1.933(3) to 2.000(3) Å (Table V). The Cu–O (N–O) distance is slightly (about 0.06 Å) longer than the Cu–O (COO) in $[Cu(L)(phen)(H_2O)]_2^{2+}$ and $[Cu(L)(phen)Br]_2$. The distances from the axial atom of the pyramid to the central Cu atom are 2.234(4) Å in **1**, 2.267(5) Å in **2**, 2.229(4) Å and 2.734(1) Å for **3**, respectively (Tables V and VI).

The metal–metal separation in the $[Cu(L)(phen)(H_2O)]_2^{2+}$ cation is 8.660, 8.656 and 8.722 Å, respectively for **1**, **2** and **3**; in the neutral $[Cu(L)(phen)Br]_2$, the Cu$\cdots$Cu distance is 8.676 Å, very close to that for the $[Cu(L)(phen)(H_2O)]_2^{2+}$ cation.

The carboxylate group in all three complexes adopts a unidentate coordination mode. The other carboxylate oxygen atom is more than 2.893(4) Å away from the copper(II) ion. This kind of coordination mode has been reported in the Cd(II) and Sn(II) complexes with isonicotinic acid N-oxide [8,9]. In all these complexes, the isonicotinic acid N-oxide ligand bridges two metal ions by using its N-O group and one of its carboxylate oxygen atoms. Neither the N-O group nor the carboxylate group is

TABLE IV   Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for non-hydrogen atoms in **3**

Atom	x/a	y/b	z/c	U_{eq} [a]
Cu(1)	6303(1)	366(1)	2831(1)	31(1)
Br(1)	5671(1)	−3431(1)	3052(1)	43(1)
Cu(2)	3832(1)	−5264(1)	2194(1)	31(1)
O(2)	5655(4)	417(3)	3936(2)	42(1)
O(3)	8406(4)	30(3)	3262(2)	40(1)
O(6)	1727(4)	−4916(2)	1788(2)	38(1)
O(5)	4385(4)	−5349(3)	1057(2)	42(1)
N(2)	4456(4)	997(3)	2459(2)	29(1)
O(10)	6883(5)	−2360(3)	1689(3)	53(1)
N(5)	5645(5)	−5935(3)	2524(2)	31(1)
O(7)	515(5)	−6468(3)	1174(2)	52(1)
N(4)	3341(5)	−5092(3)	444(2)	33(1)
N(3)	6831(5)	569(3)	1738(2)	35(1)
N(1)	6641(5)	120(3)	4537(2)	33(1)
N(6)	3300(5)	−5517(3)	3273(2)	31(1)
O(1)	4876(5)	−1137(3)	2100(3)	59(1)
O(4)	9689(5)	1568(3)	3891(3)	58(1)
C(36)	2099(6)	−5306(4)	3624(3)	39(1)
C(1)	9636(6)	724(4)	3774(3)	35(1)
C(35)	8026(6)	333(4)	1388(3)	46(1)
O(9)	11993(7)	−2686(4)	3123(3)	85(2)
C(34)	6775(6)	−6696(3)	3604(3)	34(1)
C(33)	8928(6)	−431(3)	5686(3)	31(1)
C(2)	518(6)	−5629(4)	1279(3)	33(1)
C(32)	2093(6)	−3930(3)	8(3)	38(1)
C(31)	−956(5)	−5377(3)	730(3)	28(1)
C(30)	4361(6)	−5983(3)	3664(3)	29(1)
C(29)	1124(6)	−5549(4)	−891(3)	35(1)
C(28)	3284(6)	−4176(4)	595(3)	38(1)
C(27)	7659(6)	771(4)	5296(3)	38(1)
C(26)	3343(6)	1724(3)	1351(3)	39(1)
C(25)	7775(6)	−1089(4)	4934(3)	39(1)
C(24)	6631(7)	−6960(4)	4374(3)	44(1)
C(23)	4226(6)	−6266(3)	4406(3)	36(1)
C(22)	5761(6)	1018(3)	1327(3)	32(1)
C(21)	5626(6)	−6206(3)	3258(3)	29(1)
C(20)	6646(6)	−802(4)	4363(3)	41(1)
C(19)	2142(7)	1952(4)	1789(4)	45(1)
C(18)	2335(6)	−5765(4)	−287(3)	38(1)
C(17)	5426(7)	−6752(4)	4752(3)	48(1)
C(16)	8801(6)	506(3)	5878(3)	35(1)
C(15)	3302(6)	1214(4)	2848(3)	38(1)
C(14)	7937(6)	−6922(3)	3148(3)	38(1)
C(13)	4483(6)	1248(3)	1716(3)	30(1)
C(12)	7932(6)	−6655(4)	2412(4)	42(1)
C(11)	1872(7)	−5560(4)	4366(3)	49(1)
C(10)	2130(7)	1693(4)	2531(4)	45(1)
C(9)	2913(7)	−6036(4)	4750(3)	48(1)
C(8)	6773(6)	−6154(3)	2120(3)	36(1)
C(7)	7160(8)	1009(4)	215(4)	54(2)
C(6)	3482(8)	1957(4)	567(4)	52(2)
C(5)	5870(7)	1260(4)	560(3)	44(1)
C(4)	4680(9)	1742(4)	196(4)	57(2)
C(3)	8208(8)	541(4)	620(4)	58(2)
O(8)	9566(8)	−3871(5)	3651(5)	132(3)
Br(2)	9269(1)	1618(1)	−1546(1)	68(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE V Selected bond lengths (Å) and angles (°) for **1** and **2**

Salt **1**		*Salt* **2**	
Cu(1)–O(1)	2.234(4)	Cu(1)–O(1)	2.267(5)
Cu(1)–O(2)	1.993(4)	Cu(1)–O(2)	1.987(4)
Cu(1)–O(3)	1.933(3)	Cu(1)–O(3)	1.937(3)
Cu(1)–N(2)	1.994(4)	Cu(1)–N(2)	1.999(4)
Cu(1)–N(3)	2.021(4)	Cu(1)–N(3)	2.021(4)
Hydrogen bonds		*Hydrogen bonds*	
O(1)···O(7)	2.745	O(1)···O(7)[#1]	2.831
O(1)···O(8)[#2]	2.733	O(1)···O(9)	2.732
O(5)···O(8)	2.729	O(7)···O(8)[#3]	2.798
O(3)–Cu(1)–O(2)	93.34(14)	O(3)–Cu(1)–O(2)	93.50(14)
O(3)–Cu(1)–N(2)	170.08(16)	O(3)–Cu(1)–N(2)	170.51(16)
O(2)–Cu(1)–N(2)	88.14(15)	O(2)–Cu(1)–N(2)	87.85(15)
O(3)–Cu(1)–N(3)	95.19(15)	O(3)–Cu(1)–N(3)	95.04(16)
O(2)–Cu(1)–N(3)	167.53(16)	O(2)–Cu(1)–N(3)	168.50(16)
N(2)–Cu(1)–N(3)	81.93(16)	N(2)–Cu(1)–N(3)	82.47(16)
O(3)–Cu(1)–O(1)	90.99(17)	O(3)–Cu(1)–O(1)	89.69(17)
O(2)–Cu(1)–O(1)	95.91(18)	O(2)–Cu(1)–O(1)	94.4(2)
N(2)–Cu(1)–O(1)	98.62(16)	N(2)–Cu(1)–O(1)	99.58(17)
N(3)–Cu(1)–O(1)	93.01(17)	N(3)–Cu(1)–O(1)	93.3(2)

Symmetry operators: [#1]$-1 + x, y, z$; [#2]$1 + x, y, z$; [#3]$-x, 2 - y, 1 - z$.

TABLE VI Selected bond lengths (Å) and angles (°) for **3**

[Cu(L)(Phen)(H₂O)]₂²⁺		*[Cu(L)(Phen)Br]₂*	
Cu(1)–O(1)	2.229(4)	Br(1)–Cu(2)	2.7339(8)
Cu(1)–O(3)	1.943(3)	Cu(2)–O(6)	1.944(3)
Cu(1)–O(2)	1.994(3)	Cu(2)–O(5)	2.000(3)
Cu(1)–N(2)	2.005(4)	Cu(2)–N(5)	2.008(4)
Cu(1)–N(3)	2.023(4)	Cu(2)–N(6)	2.027(4)
Hydrogen bonds			
O(1)···O(10)	2.762	O(8)···O(9)	2.917
O(1)···Br(2)[#1]	3.294	O(10)···Br(2)[#2]	3.333
O(3)–Cu(1)–O(2)	93.85(13)	O(6)–Cu(2)–O(5)	93.40(13)
O(3)–Cu(1)–N(2)	167.56(15)	O(6)–Cu(2)–N(5)	166.38(15)
O(2)–Cu(1)–N(2)	88.61(14)	O(5)–Cu(2)–N(5)	88.43(14)
O(3)–Cu(1)–N(3)	94.01(15)	O(6)–Cu(2)–N(6)	93.85(14)
O(2)–Cu(1)–N(3)	168.44(15)	O(5)–Cu(2)–N(6)	165.95(15)
N(2)–Cu(1)–N(3)	81.94(15)	N(5)–Cu(2)–N(6)	81.76(15)
O(3)–Cu(1)–O(1)	93.99(15)	O(6)–Cu(2)–Br(1)	94.71(11)
O(2)–Cu(1)–O(1)	95.40(16)	O(5)–Cu(2)–Br(1)	95.32(11)
N(2)–Cu(1)–O(1)	97.92(15)	N(5)–Cu(2)–Br(1)	98.56(11)
N(3)–Cu(1)–O(1)	92.49(16)	N(6)–Cu(2)–Br(1)	96.07(11)

Symmetry operators: [#1]$1 - x, -y, -z$; [#2]$2 - x, -y, -z$.

involved in coordination with metal ion in $[M(H_2O)_6]L_2$ ($M = Co$, Ni, Zn) [6,9]. In $[Cu(H_2O)(Py)(L)_2]$ (Py = pyridine), the L ligand coordinates with the copper(II) ion unidentately (using one carboxylate oxygen atom), whereas in $Cu(H_2O)_2(L)_2$, the ligand is bidentate, chelating with one Cu–O (COO) bond significantly elongated (2.691(4) Å) [5]. Another coordination mode reported involves linkage of two metal
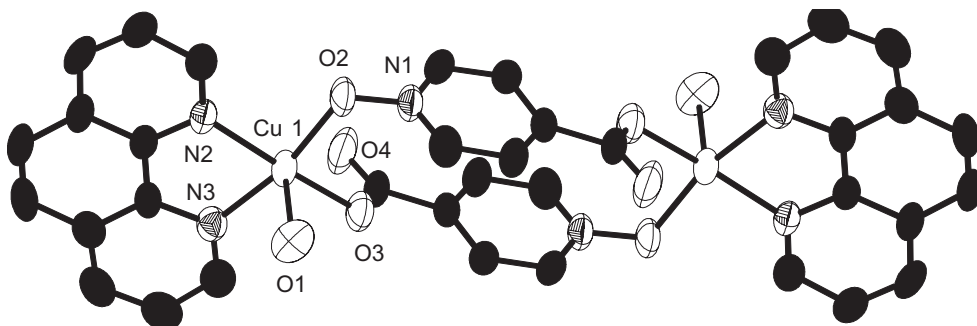
FIGURE 1   Perspective view of $[Cu(L)(phen)(H_2O)]_2^{2+}$ in **1** with atomic labelling. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

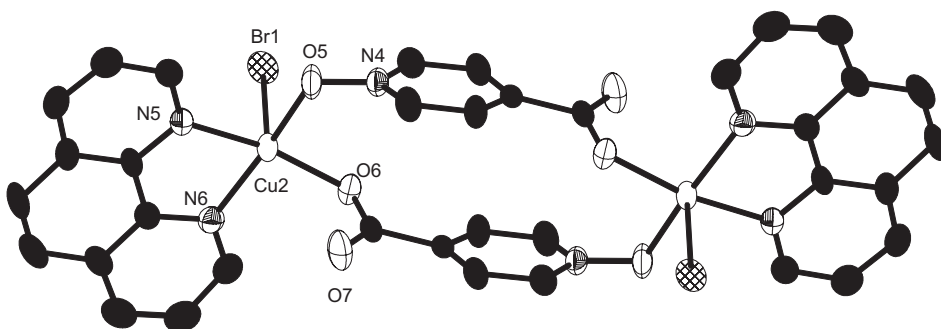FIGURE 2   Perspective view of $[Cu(L)(phen)Br]_2$ in **3** showing the atom labelling. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

ions by a bidentate bridging carboxylate group in trinuclear and tetranuclear Cu(II) complexes and lanthanide complexes [6].

Hydrogen bonds are formed within **1**, **2** and **3**. In **1**, a number of hydrogen bonds among nitrate group, lattice and coordination water molecules (see Table V), result in a 2D layer parallel to (001) planes (Fig. 3). The hydrogen bonds in **2** and **3** are much simpler (see Tables V and VI), and the Cu_2 dimer rings are not interconnected via hydrogen bonds. As shown in Fig. 4, the aqua ligand in **2** forms hydrogen bonds with a lattice water molecule and an oxygen atom of the perchlorate anion. In complex **3**, hydrogen bonds are formed among the aqua ligand, a bromide anion and lattice water molecules.

ESR Spectra and Magnetic Properties

As is typical for EPR spectra of Cu(II) species, the three Cu(II) salts exhibit an axial g tensor, with $g_{\parallel}$ values of 2.2581, 2.2505 and 2.2520 for **1**, **2** and **3**, respectively. The $g_{\perp}$ values are 2.0582, 2.0581 and 2.0552, respectively for **1**, **2** and **3**. These values agree well with literature data [12].

The plot of $1/\chi_M$ as a function of temperature for the three salts is shown in Fig. 5. Results indicate that all three Cu(II) complexes are Curie–Weiss paramagnetic, with little interaction between the two metal centers within a dinuclear unit, as supported
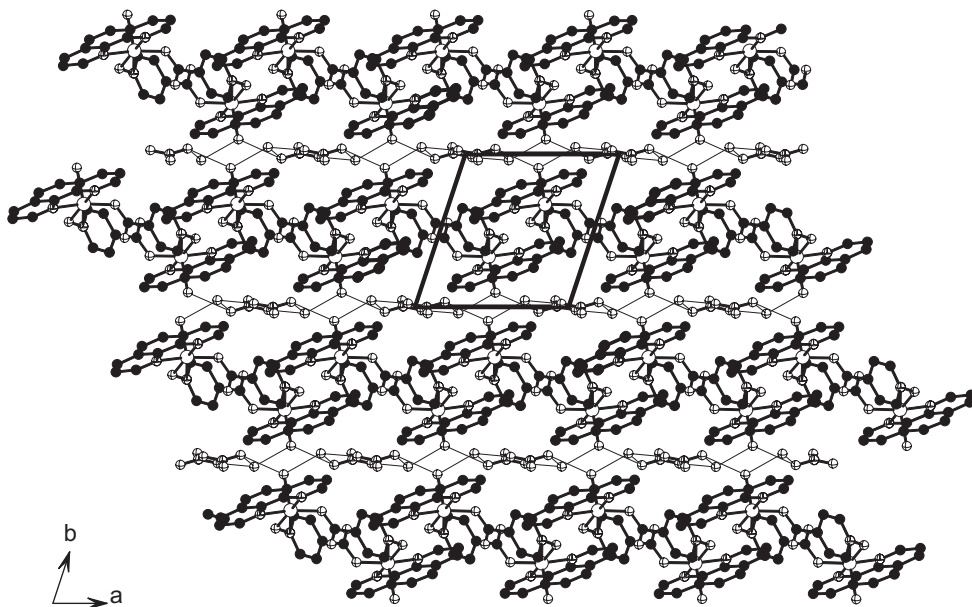
FIGURE 3 Hydrogen-bonded 2D layer along (001) plane in **1**. Hydrogen bonds are shown as broken lines.
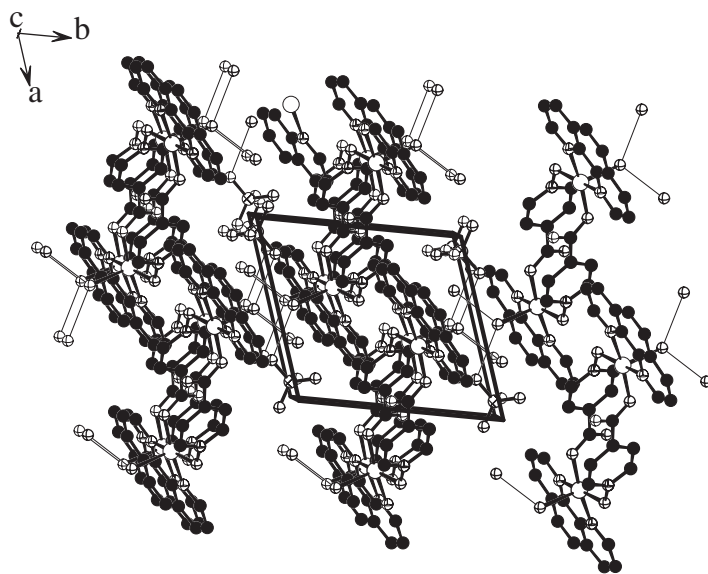

FIGURE 4 View of structure of **2** down the *c*-axis. Hydrogen bonds are shown as broken lines.

by the small values of the Weiss constants [0.11(2), 0.17(2) and 0.03(3) K for complexes **1**, **2** and **3**, respectively]; the two Cu(II) centers are over 8.6 Å away from each other. The effective magnetic moments (μ_{eff}) per formula unit are 2.503(1) μ_B, 2.438(1) μ_B and 3.531(2) μ_B, respectively for complexes **1**, **2** and **3**, which correspond to 2, 2 and 4
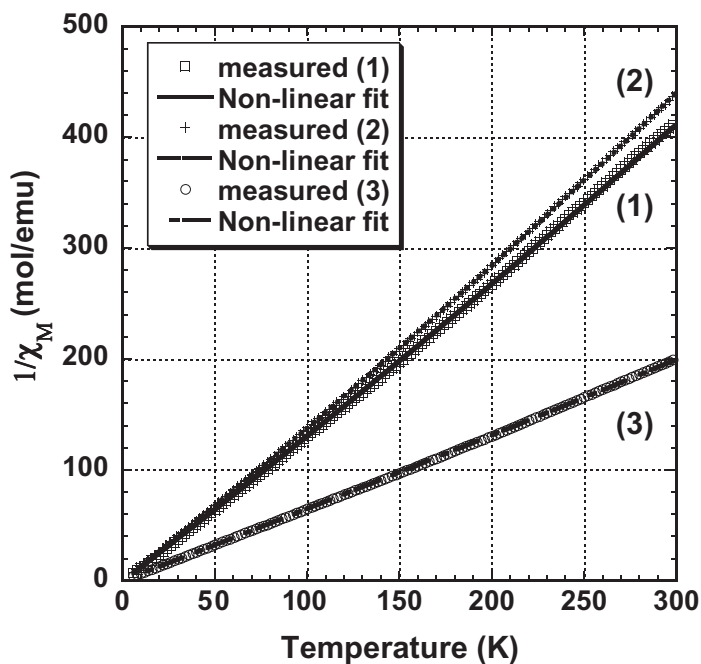
FIGURE 5   Plot of $1/\chi_{M}$ as a function of temperature for **1**, **2** and **3**.

isolated single-spin Cu(II) ions per formula unit. These experimental results are in good agreement with the theoretical values.

Acknowledgements

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