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Novel copper(II) complexes with diazamesocyclic ligands functionalized by additional donor group(s): syntheses, crystal structures and magnetic properties

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Copper(II) complexes with three diazamesocyclic ligands based on l,5-diazacyclooctane (DACO) bearing additional imidazole or phenol functional donor groups, 1,5-bis(imidazol-4-ylmethyl)- (**L**^{1}), 1-(imidazol-4-ylmethyl)- (**L**^{2}), and 1-(2-hydroxybenzyl)-1,5-diazacyclooctane (**HL**^{3}), have been newly synthesized and characterized, and their structures determined by X-ray diffraction analyses. It has been revealed that with $Cu(ClO_4)_2\cdot 6H_2O$ **L**^{1} forms a mononuclear complex $[CuL^1Cl]ClO_4\cdot H_2O$ **1**, **L**^{2} forms a μ-Cl^- bridged binuclear complex $[CuL^2Cl]_2[ClO_4]_2$ **2**, whereas **HL**^{3} forms a phenoxo-bridged binuclear complex $[CuL^3(H_2O)]_2[ClO_4]_2$ **3**. Each Cu^{II} in the three complexes is five-coordinated in a distorted square-pyramidal environment. For the mononuclear complex **1** the Cl^- anion is at the apical site, whereas for the μ-Cl^--bridged binuclear complex **2** the two bridging Cl^- anions occupy both the axial and one equatorial position with Cu–Cl–Cu angle 88.81(5)° and intramolecular Cu · · · Cu separation 3.494(8) Å. In the phenoxo-bridged binuclear complex **3** the Cu–O–Cu bridging angle is 100.80(12)° and the intramolecular Cu · · · Cu distance is 3.0324(9) Å. Variable-temperature magnetic susceptibility measurements on the two binuclear complexes **2** and **3** in the range 4.2–300 K indicate a quite different magnetic intramolecular coupling between the binuclear copper(II) centers, from a weak ferromagnetic to a very strong antiferromagnetic coupling, with $2J = 1.16$ (for **2**) *vs.* -574 cm^{-1} (for **3**), and the magneto-structural correlations are discussed in detail. The solution behaviors of the complexes have been further studied by UV/Vis and ESR techniques.

Introduction

Macrocyclic polyamines, especially the tri- and tetra-amines, and their metal complexes have been the subject of extensive studies for several decades.[1–3] Mesocyclic diamines, which have two nitrogen donors with potential bidentate chelating ligands and offer the potential ability for further functionalization,[4] are some of the smallest members of the family of cyclic polyamines. 1,5-Diazacyclooctane (DACO) is a typical example of diazamesocycles, which usually shows an interesting "boat/chair" configuration when it binds to metal ions which blocks sixth coordination at the apical site.[5] So far, some derivatives of DACO bearing donor pendants and their metal complexes have been reported,[4–7] and the metal complexes with such functionalized ligands were shown by Darensbourg *et al.* to have very interesting properties and functions.

In our efforts[7] systematically to investigate control of the structures and properties (especially the magnetic properties of binuclear or polynuclear complexes) as well as the coordination chemistry of diazamesocyclic ligands by modification of their backbone, we reported a variation of the coordination modes and magnetic properties of copper(II) complexes with DACO by altering donor pendants on it.[7f] As a continuation of our efforts, we report herein the crystal structures, characterization, solution behaviors and magnetic properties of three novel copper(II) complexes with DACO ligands functionalized by imidazole or phenol donor group(s) (see Chart 1). Quite different magnetic properties were found to exist in the two binuclear complexes. The general rules for the coordination modes of copper(II) complexes with DACO ligands containing various pendants and the magneto-structural correlations of the binuclear copper(II) complexes are discussed.

Experimental

Materials and general methods

The starting compounds, DACO·2HBr,[8a,b] 4-chloromethylimidazole hydrochloride,[8c] and 1-(2-hydroxybenzyl)-1,5-diazacyclooctane (**HL**^{3})[7f] were prepared according to the literature methods. All other reagents and solvents for syntheses and analyses were of analytical grade. FT-IR spectra (KBr pellets) were taken on a FT-IR 170SX (Nicolet) spectrometer and electronic absorption spectra on a Shimadzu UV-260 spectrophotometer. Carbon, hydrogen, and nitrogen analyses were performed on a Perkin-Elmer 240C analyzer. Conductivities of the complexes were measured at room temperature using a DDS 11A conductometer. ^{1}H NMR spectra were recorded on a Bruker AC-P 200 spectrometer (200 MHz) at 25 °C with tetramethylsilane as the internal reference, solution and solid state (polycrystalline) EPR spectra (X band) on a Bruker ER-200-DSRC10 spectrophotometer.

Syntheses of ligands

1,5-Bis(imidazol-4-ylmethyl)-1,5-diazacyclooctane tetrahydrochloride monohydrate (L^1·4HCl·H$_2$O). A suspension of DACO (2.64 g, 9.63 mmol) and KOH (1.11 g, 19.7 mmol) in anhydrous ethanol (60 mL) was stirred for 2 h at room temperature. Then 4-chloromethylimidazole hydrochloride (4.88 g, 24.0 mmol) and triethylamine (3.25 g, 23.4 mmol) in anhydrous ethanol (25

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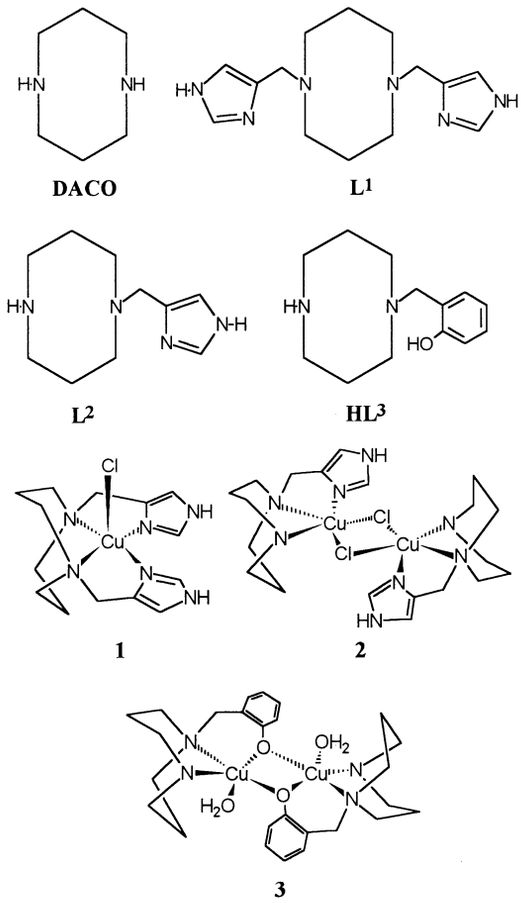

Chart 1

mL) were added dropwise in 2 h. When the addition was complete 8 mL triethylamine were added and stirring was continued for 24 h at room temperature. After the solvent was removed under reduced pressure, the residue was dissolved in water (20 mL) and the pH adjusted to *ca.* 10 with K_2CO_3. The aqueous phase was extracted with $CHCl_3$ (100 mL × 5), the combined organic phase evaporated under vacuum and the crude product purified by silica gel column chromatography (CH_2Cl_2:MeOH:$NH_3{\cdot}H_2O$ = 10:10:1), to obtain the acid-free ligand as a colorless oil. This material was further purified by conversion into the HCl salt to obtain a white crystalline material. Yield 3.17 g (75% based on DACO) (Found: C, 38.30; H, 6.65; N, 19.46%. Calc. for $C_{14}H_{22}N_6{\cdot}4HCl{\cdot}H_2O$: C, 38.37; H, 6.44; N, 19.18%). ^{1}H NMR (D_2O): δ 2.08 (m, 4H), 3.29 (t, 8H, J = 5.4 Hz), 4.37 (s, 4H), 7.65 (s, 2H) and 8.73 (s, 2H). IR (KBr pellets, cm^{-1}): 2984w, 1618m, 1462m, 1436m, 1331w, 1084w, 965w and 627s.

1-(Imidazol-4-ylmethyl)-1,5-diazacyclooctane trihydrochloride dihydrate ($L^2{\cdot}3HCl{\cdot}2H_2O$). A solution of DACO·2HBr (7.26 g, 26.5 mmol) and potassium hydroxide (3.13 g, 55.7 mmol) in anhydrous methanol (40 mL) was stirred for 4 h at room temperature. Then a solution of 4-chloromethylimidazole hydrochloride (1.34 g, 6.6 mmol) in anhydrous ethanol was added dropwise. The resulting mixture was heated at reflux for 1 h, followed by stirring at room temperature overnight. The solvent was removed under reduced pressure, the residue dissolved in water (20 mL) and the pH adjusted to *ca.* 9 with Na_2CO_3. The aqueous phase was extracted with $CHCl_3$ (100 mL × 5), and the combined $CHCl_3$ phase then dried and evaporated. The residue was purified by column chromatography on silica gel by eluting with CH_2Cl_2:MeOH:$NH_3{\cdot}H_2O$ (from 10:5:1 to 5:5:1). The oily product was dissolved in anhydrous ethanol, and the final product obtained as a pale white solid by blowing HCl gas into the solution. Yield: 1.3 g (55% based on 4-chloromethylimidazole hydrochloride) (Found: C, 32.41; H, 7.47; N, 14.97%. Calc. for $C_{12}H_{19}N_3{\cdot}3HCl{\cdot}2H_2O$: C, 32.66; H, 7.40; N, 15.24%). ^{1}H NMR (D_2O): δ 2.20 (m, 4H), 3.30 (t, 4H, J = 5.6), 3.42 (t, 4H, J = 6.4 Hz), 4.47 (s, 2H), 7.69 (s, 1H) and 8.73 (s, 1H). IR (KBr pellets, cm^{-1}): 3423m, 2981m, 1616vs, 1599m, 1556s, 1523m, 1466m, 1437w, 1332w, 1274m, 1143m, 1067m and 789s.

Preparation of complexes

The mononuclear complex **1**, $[CuL^1Cl]ClO_4{\cdot}H_2O$, was prepared by mixing $Cu(ClO_4)_2{\cdot}6H_2O$ (185 mg, 0.5 mmol) and $L^1{\cdot}4HCl{\cdot}H_2O$ (184 mg, 0.5 mmol) in water. The pH value of this solution was adjusted to *ca.* 7–8 with dilute NaOH aqueous solution. The reaction mixture was filtered and left to stand at room temperature. Blue single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent. Yield: 172 mg (70%) (Found: C, 34.11; H, 5.18; N, 16.97%. Calc. for $C_{14}H_{24}Cl_2CuN_6O_5$: C, 34.26; H, 4.93; N, 17.13%). FT-IR (KBr pellet, cm^{-1}): 3397br, 2901w, 1618w, 1593s, 1481ms, 1458m, 1357s, 1104vs and 620vs. Λ_M (MeOH): 108 Ω^{-1} cm^2 mol^{-1}. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (MeOH): 594 (172) and 264 (4400).

The μ-Cl^- bridged binuclear complex **2**, $[CuL^2Cl]_2[ClO_4]_2$, was obtained in a procedure similar to the preparation of **1**. Yield: 66% (Found: C, 30.24; H, 4.85; N, 14.19%. Calc. for $C_{20}H_{36}Cl_4Cu_2N_8O_8$: C, 30.58; H, 4.62; N, 14.27%). FT-IR (KBr pellet, cm^{-1}): 3287w, 2958m, 1591s, 1498vs, 1479m, 1459m, 1433w, 1102vs and 623s. Λ_M (MeOH): 205 Ω^{-1} cm^2 mol^{-1}. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (MeOH): 629 (264) and 256 (7250).

The phenoxo-bridged binuclear complex **3**, $[CuL^3(H_2O)]_2[ClO_4]_2$, was synthesized by mixing $Cu(ClO_4)_2{\cdot}6H_2O$ (111 mg, 0.3 mmol) and HL^3 (66 mg, 0.3 mmol) in acetone–water. The reaction mixture was filtered and green single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the solvent. Yield: 62 mg (52%) (Found: C, 38.75; H, 5.45; N, 6.79%. Calc. for $C_{13}H_{21}ClCuN_2O_6$: C, 39.00; H, 5.29; N, 7.00%). FT-IR (KBr pellet, cm^{-1}): 3457br, 3252w, 2957w, 1702vs, 1635m, 1598s, 1576m, 1484vs, 1364s, 1262s, 1097vs and 622s. Λ_M (MeOH): 187 Ω^{-1} cm^2 mol^{-1}. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (MeOH): 637 (468), 428 (1346), 281 (10680), 234 (12090), 208 (14880) and 202 (14280).

CAUTION: although no problems were encountered in this work, transition metal perchlorate complexes are potentially explosive and should be handled with proper precautions.

Magnetic study

The variable temperature magnetic susceptibilities for complexes **2** and **3** were measured on a SQUID magnetometer in the 4.2–300 K temperature range. The susceptibilities were corrected for diamagnetism with Pascal's constants for all the constituent atoms, and magnetic moments calculated by the equation $\mu_{eff} = 2.828(\chi_m T)^{1/2}$.

Crystallographic study

The reflection data were collected on an Enraf-Nonius CAD-4 (for complex **1**), Siemens P4 (for **2**) or Bruker Smart 1000 CCD X-ray diffractometer (for **3**). The determination of unit cell parameters and data collections were performed with Mo-Kα radiation (λ = 0.71073 Å). All structures were solved by direct methods and empirical (for **1**) or semi-empirical (for **2** and **3**) absorption corrections applied. All non-hydrogen atoms and most hydrogen atoms in **2** were determined by successive Fourier syntheses and refined isotropically. The final refinement was done by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F (for **1**) or F^2 (for **2** and **3**).[9] Most hydrogen atoms were added theoretically riding on the concerned atoms and refined with fixed thermal factors for **1** and **3**. The crystallographic data and refinement details for the complexes are summarized in Table 1.

CCDC reference number 186/2311.

See http://www.rsc.org/suppdata/dt/b0/b007424l/ for crystallographic files in .cif format.

Results and discussion

Syntheses and general characterization

The doubly substituted ligand **L**[1] was prepared by using an excess of 4-chloromethylimidazole hydrochloride, and an excess of DACO was used to obtain the monoalkylated product **L**[2]; both were purified by silica gel column chromatography. Acid-free ligands **L**[1] and **L**[2] were obtained as oils so that they were converted into the HCl salts to obtain crystalline solids. The yields for both ligands are over 55% and all the analytical data are in good agreement with the theoretical requirements.

The syntheses of the complexes were achieved by reactions of the corresponding acid-free ligands (**L**[1]·4HCl·H_2O and **L**[2]·3HCl·$2H_2O$ were neutralized with NaOH aqueous solution prior to complexation) or the "free" ligand (**HL**[3]) with $Cu(ClO_4)_2·6H_2O$. The electrical conductance values in methanol solution indicate that **1** behaves as a 1 : 1, **2** and **3** as 2 : 1 electrolytes,[10] consistent with their crystal structures. The IR spectra show absorption bands resulting from the skeletal vibrations of the aromatic ring in the 1400–1600 cm^{-1} region, and bands of ClO_4^- appear at 1104–1097 and 623–620 cm^{-1} for all the complexes. In addition, there is a broad band centered at 3397 and 3457 cm^{-1} due to the stretching of the water molecules for **1** and **3**, and a weak but sharp band at 3287 and 3252 cm^{-1} due to the N–H stretching of DACO for **2** and **3**, respectively.

Description of the crystal structures

Mononuclear copper(II) complex 1. The crystal structure along with the atomic numbering scheme of complex **1** is shown in Fig. 1(a), and selected bond distances and angles relevant to the copper(II) coordination sphere are listed in Table 2. The structure of **1** consists of a discrete $[Cu\mathbf{L}^1Cl]^+$ cation and a perchlorate counter anion. The Cu^{II} is coordinated by two nitrogen atoms of the imidazole pendant and a pair of nitrogen donors of the DACO ring. A chloride anion completes the coordination polyhedron around the central Cu^{II}. The coordination polyhedron (CuN_4Cl) could be best described as a square pyramid with a chloride anion occupying the axial position, which is reflected by the τ value (0.02) defined by Addison *et al.* ($\tau = 0$ for an ideal square pyramid, and 1 for an ideal trigonal bipyramid).[12,13] The central Cu^{II} is 0.364 Å above the basal least-squares plane defined by N(1), N(2), N(3) and N(5), towards the apical Cl(1) anion, and the dihedral angle between the two imidazole rings is 17.0(4)°.

The two $Cu–N_{DACO}$ bond distances are nearly the same (2.063(8) *vs.* 2.070(7) Å), both being normal Cu–N coordination bonds.[14] The $Cu–N_{im}$ bond distances are also similar (1.974(8) *vs.* 1.978(7) Å) and a little shorter than the $Cu–N_{DACO}$ bonds, indicating stronger coordination. The apical Cu–Cl(1) bond (2.477(3) Å) is a little longer than Cu–Cl bonds observed in similar complexes,[15,16] indicating weaker coordination. The weakly coordinating Cl^- anion might be exchanged by other molecules or ions, so the complex might be applicable in homogeneous catalysis, or as a functional building block for the construction of larger architectures.

In complex **1** **L**[1] acts as a tetradentate chelating agent, and a pair of nitrogen atoms of the DACO ring and two nitrogen donors of the imidazole pendants are in *cis* position in the coordination polyhedron, which affects the coordination geometry around Cu^{II}. The DACO ring of the ligand takes the "boat/chair" configuration and is bent such that the central methylene C–H group of the boat form of the metalladiazacyclohexane rings shields the metal center in the complex with a H···Cu distance of 2.482(6) Å and a H–Cu–apex angle of 8.1(3)°. Thus this hydrogen atom of methylene effectively blocks the sixth coordination site resulting in this five-coordinated copper(II) complex.

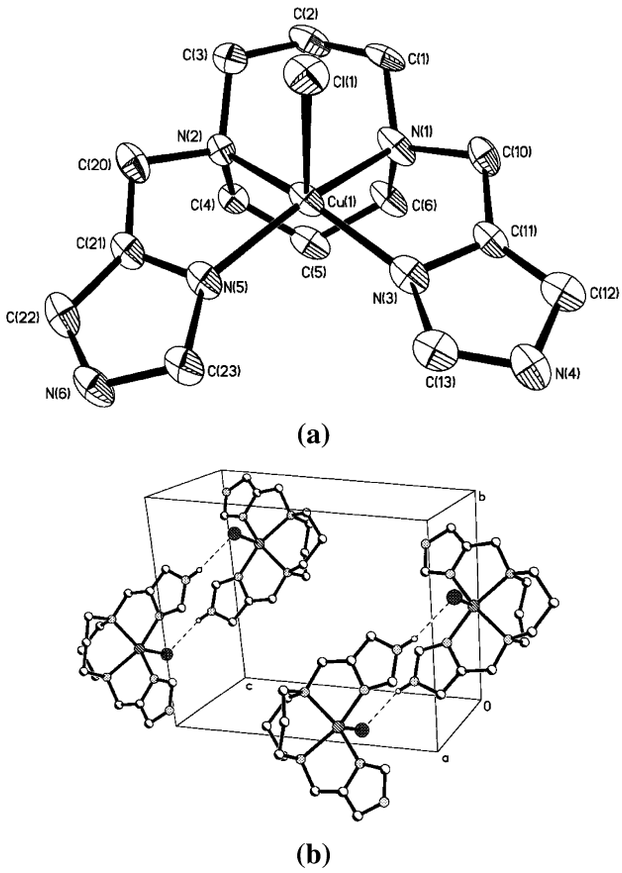

Fig. 1 (a) The ORTEP[11] view of complex **1** with 35% probability thermal ellipsoids; (b) stacking diagram of **1** in the unit cell showing the hydrogen bonding connected dimeric structure.

In addition, the N···Cl separation is 3.145(7) Å with H···Cl (symmetry code: $1 - x$, y, z) 2.336(3) Å (bond angle: 149.5(4)°), indicating the existence of N–H···Cl hydrogen bonds[17] between the axial chloride anion and the uncoordinated N–H group of the imidazole ring, by which a dimer of two adjacent ligands is formed in the unit cell as depicted in Fig. 1(b), and the complex may thus be stabilized.

The μ-Cl^- bridged binuclear complex 2. An ORTEP view of complex **2** including the atomic numbering scheme is shown in Fig. 2 and selected bond lengths and angles are listed in Table 3. **2** consists of a discrete $[Cu\mathbf{L}^2Cl]_2^{2+}$ cation and two perchlorate anions. In the $[Cu\mathbf{L}^2Cl]_2^{2+}$ cation, which results from the pairing of two mononuclear units related by a crystallographic center of symmetry, the two Cu^{II} are bridged equivalently by two chloride anions. Each is bound to **L**[2] by one nitrogen atom of the pendant imidazole group and two nitrogen donors of the DACO ring, which also takes a "boat/chair" configuration. Two bridging chloride anions complete the coordination polyhedron around each Cu^{II}. The coordination polyhedron (CuN_3Cl_2) can be best described as a distorted square pyramid with $\tau = 0.30$. The Cu^{II} is 0.278(5) Å above the mean basal plane formed by N(1), N(2), N(3) and Cl(1), towards the apical Cl^- anion and the axial Cu(1)–Cl(1a) distance is *ca.* 0.33 Å longer than the Cu(1)–Cl(1) bond distance in the basal plane (2.6571(14) *vs.* 2.3248(14) Å) probably due to the Jahn–Teller effect. The Cu^{II} and chloride anions form a rhombic plane with angles of 91.19(5)° for Cl(1)–Cu(1)–Cl(1)#1 and 88.81(5)° for Cu(1)–Cl(1)–Cu(1)#1, respectively. The intramolecular Cu···Cu non-bonding distance in the dimer is 3.494(8) Å, which is close to those in other chloro-bridged binuclear copper(II) complexes.[17]

In complex **2** one oxygen atom of the perchlorate anion forms a hydrogen bond (2.865(4) Å) with the uncoordinated

Table 1 Crystallographic data and the structure refinement summary for complexes **1**, **2** and **3**

	1	**2**	**3**
Chemical formula	$C_{14}H_{24}Cl_2CuN_6O_5$	$C_{20}H_{36}Cl_4Cu_2N_8O_8$	$C_{26}H_{42}Cl_2Cu_2N_4O_{12}$
M	490.83	785.47	800.62
T/K	299(1)	299(1)	293(2)
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	$Pbcn$
a/Å	7.529(2)	8.5280(4)	19.0196(18)
b/Å	11.343(5)	8.8165(7)	10.1623(9)
c/Å	12.362(2)	10.1276(5)	16.6277(16)
α/°	82.21(3)	86.862(7)	
β/°	72.49(3)	82.350(6)	
γ/°	82.34(3)	89.608(6)	
V/Å^3	992.7(5)	753.56(1)	3213.9(5)
Z	2	1	4
μ/cm^{-1}	1.411	3.017	1.557
Measured reflections	2734	3959	12373
Unique reflections	2472	3283	2822
$R(R_{int})$	0.078 (0.08)	0.0572 (0.0258)	0.0433 (0.0330)
R_w	0.078	0.0837	0.1230

Table 2 Selected bond distances (Å) and angles (°) for complex **1**

Cu(1)–Cl(1)	2.477(3)	Cu(1)–N(1)	2.063(8)
Cu(1)–N(2)	2.070(7)	Cu(1)–N(3)	1.974(8)
Cu(1)–N(5)	1.978(7)		
N(1)–Cu(1)–N(2)	85.9(3)	N(1)–Cu(1)–N(3)	83.5(3)
N(2)–Cu(1)–N(5)	83.4(3)	N(3)–Cu(1)–N(5)	99.8(3)
N(2)–Cu(1)–N(3)	158.6(4)	N(1)–Cu(1)–N(5)	157.4(4)
Cl(1)–Cu(1)–N(1)	98.3(2)	Cl(1)–Cu(1)–N(2)	101.8(2)
Cl(1)–Cu(1)–N(3)	98.1(3)	Cl(1)–Cu(1)–N(5)	103.3(3)

Table 3 Selected bond distances (Å) and angles (°) for complex **2**

Cu–N(1)	2.073(4)	Cu–N(2)	1.998(5)
Cu–N(3)	1.975(4)	Cu–Cl(1)	2.3248(14)
Cu–Cl(1)#1	2.657(2)	Cu(1)···Cu(1)#1	3.494(8)
N(3)–Cu–N(2)	154.2(2)	N(3)–Cu–N(1)	82.9(2)
N(2)–Cu–N(1)	85.8(2)	N(3)–Cu–Cl(1)	96.47(13)
N(2)–Cu–Cl(1)	91.64(14)	N(1)–Cu–Cl(1)	172.36(11)
N(3)–Cu–Cl(1)#1	97.79(14)	N(2)–Cu–Cl(1)#1	106.5(2)
N(1)–Cu–Cl(1)#1	96.45(11)	Cl(1)–Cu–Cl(1)#1	91.19(5)
Cu–Cl(1)–Cu#1	88.81(5)		

Symmetry transformation used to generate equivalent atoms (#1): $-x$, $-y-1$, $-z+1$.

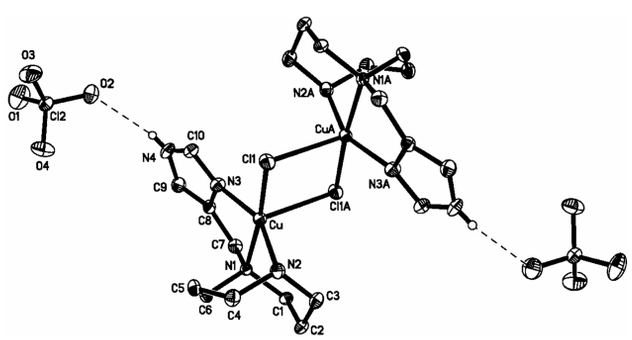

Fig. 2 The ORTEP view of complex **2** with 30% probability thermal ellipsoids.

nitrogen donor of the pendant imidazole as shown in Fig. 2. The H···O separation is 2.233(5) Å and the N–H···O bond angle 154.8(3)°.

The phenoxo-bridged binuclear complex 3. An ORTEP view of complex **3** including the atomic numbering scheme is given in Fig. 3(a), and relevant bond distances and angles are listed in Table 4. This complex consists of a discrete $[CuL^3(H_2O)]_2^{2+}$

Table 4 Selected bond distances (Å) and angles (°) for complex **3**

Cu(1)–O(1)#1	1.967(3)	Cu(1)–O(1)	1.969(3)
Cu(1)–N(2)	2.001(4)	Cu(1)–N(1)	2.014(3)
Cu(1)–O(2)	2.349(4)	Cu(1)···Cu(1)#1	3.0324(9)
O(1)#1–Cu(1)–O(1)	79.20(12)	O(1)#1–Cu(1)–N(2)	96.45(14)
O(1)–Cu(1)–N(2)	155.44(14)	O(1)#1–Cu(1)–N(1)	173.49(12)
O(1)–Cu(1)–N(1)	94.86(12)	N(2)–Cu(1)–N(1)	87.86(15)
O(1)#1–Cu(1)–O(2)	88.82(15)	O(1)–Cu(1)–O(2)	88.51(16)
N(2)–Cu(1)–O(2)	115.73(18)	N(1)–Cu(1)–O(2)	93.71(16)
Cu(1)#1–O(1)–Cu(1)	100.80(12)		

Symmetry transformation used to generate equivalent atoms (#1): $-x+1$, $-y$, $-z+2$.

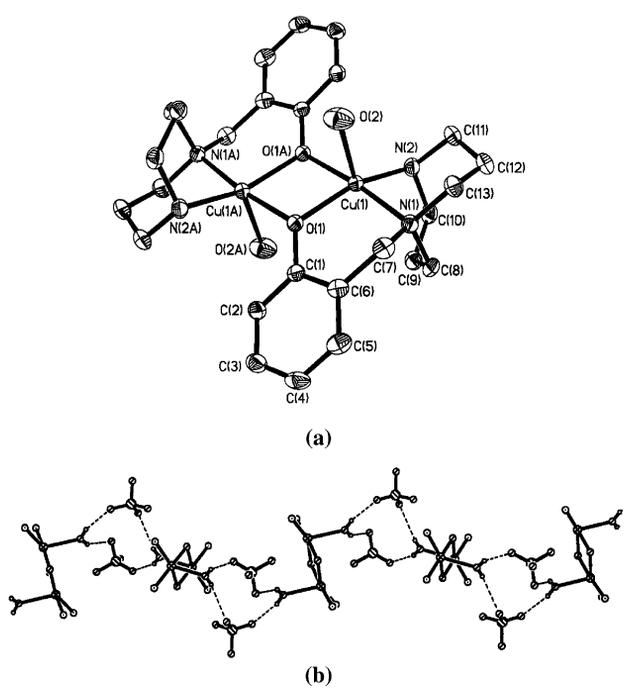

Fig. 3 (a) The ORTEP view of complex **3** with 30% probability thermal ellipsoids; (b) a view of the one-dimensional structure in **3** along the c axis (only the coordination environments of Cu^{II} are retained for clarity) linked by hydrogen bonding.

cation and two perchlorate anions. The two mononuclear units are related by a crystallographic center of symmetry. Each Cu^{II} is in a distorted square-pyramidal coordination environment with $\tau = 0.30$. Two bridging oxygen atoms from the deprotonated pendant phenol groups and two nitrogen donors of the

DACO ring of $\mathbf{L^3}$ comprise the basal plane, and each axial coordination site is occupied by one oxygen atom of water. The Cu(1) ion deviates by *ca.* 0.25 Å from the basal mean equatorial plane of the square pyramid (N(1)–N(2)–O(1)–O(1a)) towards the apical O(2).

The two Cu^{II} are bridged equivalently by two phenoxo bridges. The bridging oxygen anions are bound asymmetrically to Cu^{II} at almost the same distances of 1.967(3) *vs.* 1.969(3) Å, respectively. The Cu–O–Cu bridging angle is 100.80(12)° and the two phenol rings of $\mathbf{L^3}$ are parallel to each other. The two Cu^{II} are separated by 3.0324(9) Å, which is similar to distances observed for other binuclear copper(II) complexes with phenoxo bridging at the two equatorial positions.[19] In our previous work, an azide-bridged binuclear copper(II) complex of the same ligand ($\mathbf{L^3}$) has been reported.[7f] It can be obtained directly from **3** by adding stronger azide donors, which act as two end-on bridges to form a binuclear complex which exhibits intramolecular ferromagnetic coupling between the two Cu^{II}.

An important feature of complex **3** to be noted is that each $[Cu\mathbf{L^3}(H_2O)]_2^{2+}$ unit carries four perchlorate ions which are hydrogen bonded to the coordination water molecules and each perchlorate anion acts as a hydrogen bond acceptor with two adjacent cations, providing a μ-ClO_4^- bridged linear zigzag structure in the unit cell (Fig. 3b). These hydrogen bonds form a ring system consisting of two water molecules and two perchlorate ions. However these bonds are relatively weak, with interatomic distances of 3.089(4) *vs.* 2.856(5) Å for O(2)···O(4) and O(2)···O(6), both being in the range of weak hydrogen bond distances.[17] Furthermore, the H···O separations are 2.491(4) *vs.* 2.088(3) Å and hydrogen bond angles are 146.23(5) *vs.* 159.88(6)°, respectively.

Based on these findings and our previous results for copper(II) complexes with DACO ligands bearing one or two functional quinoline, imidazole, pyridine, or phenol pendant(s), we could find a general rule for the coordination modes of Cu^{II} as follows: doubly substituted tetradentate heterocyclic ligands tend to form stable five-coordinated mononuclear complexes (except for a ligand with two sterically bulky quinoline pendants forming a square-planar complex due to the stereochemical influence[7b]). Furthermore, it was clearly evidenced that the degree of distortion increases with the size of the heterocyclic pendants. However, monosubstituted tridentate heterocyclic ligands tend to form chloro-bridged binuclear or linear complexes with Cu^{II}, and each Cu^{II} is also in a five-coordinated geometry. For a DACO ligand with two phenol pendants a phenoxo-bridged trinuclear complex was obtained, whereas the monosubstituted ligand can form a phenoxo-bridged binuclear complex. Thus mono-, bi-, tri-, and polynuclear five-coordinated Cu^{II} have been systematically and conveniently achieved by altering the pendants on DACO.

Electronic and ESR spectra

The UV-Vis spectral data for complexes **1**–**3** in methanol solution show absorption maxima at 594, 629, and 637 nm, respectively, which are in agreement with those of other five-coordinated copper(II) complexes with similar geometries. Complexes **2** and **3** display a slightly higher λ_{max} than that of **1**, suggesting more distortion toward a trigonal bipyramid.[20] This is consistent with the degree of distortion found in the X-ray structural analysis. This spectral feature is typical of five-coordinated copper(II) complexes with distorted square-pyramidal geometry which generally exhibit a band in the 550–660 nm range (d_{xz}, $d_{yz} \longrightarrow d_{x^2-y^2}$).[20,21] In addition, complex **3** exhibits one strong ligand-to-metal charge transfer (LMCT) band toward higher energy at 428 nm.[22] The electronic spectra of all the complexes display characteristic absorptions at 200–300 nm assigned to ligand $\pi \longrightarrow \pi^*$ transitions.

The X-band ESR spectra of the mononuclear copper(II) complex **1** were measured in the solid polycrystalline state and in methanol solution at room temperature and 110 K, respectively. The following parameters were obtained for the polycrystalline powder at room temperature: $g_z = 2.24$, $g_y = g_x = 2.06$. The resolution was not improved very much upon cooling to 110 K with $g_z = 2.26$, $g_y = g_x = 2.10$. The g values have the relationship: $g_\parallel > g_\perp > g_e$, which indicates that the 3d unpaired electron of the Cu^{II} should occupy the $d_{x^2-y^2}$ orbital and a dominantly tetragonal component in the solid stereochemistry.[23,24] The equal values of g_x and g_y imply that the ground-state wavefunction is nearly pure $d_{x^2-y^2}$, and contains no contributions of d_{z^2} due to the higher symmetry of the coordination polyhedron, which is consistent with the crystal structure data. The room-temperature solution spectra show hyperfine splitting lines characteristic of copper(II) complexes, which were also observed with a frozen solution of **1**. The approximate ESR parameters obtained are $g_{iso} = 2.10$ ($A_{iso} = 82$ G), $g_\parallel = 2.17$ ($A_\parallel = 177$ G), and $g_\perp = 2.06$ ($A_\perp = 35$ G), where $g_\perp = (3g_{iso} - g_\parallel)/2$ and $A_\perp = (3A_{iso} - A_\parallel)/2$.[3b] They have the relationship $g_\parallel > g_\perp > g_e$, and a larger $A_\parallel$ value, indicating smaller distortion in the coordination geometry of the Cu^{II} away from the square pyramid in solution,[25] similar to the geometry in the solid state.

The X-band ESR spectra of complexes **2** and **3** in the solid state at room temperature show isotropic characters with $g_{av} = 2.04$ (for **2**) and 2.17 (for **3**), probably owing to exchange narrowing. No absorption is observed at half-field ($\Delta m_s = 2$, $g = 4$) indicating a small zero field splitting effect.[26] The frozen solution spectra of **2** and **3** in methanol solution also exhibit only a quasi-isotropic feature, and the g value (2.05 *vs.* 2.16) is nearly the same as that of the polycrystalline sample, indicating that there is no significant change of the coordination environment under the two conditions.

Magnetochemistry of the binuclear complexes 2 and 3

The magnetic behavior of complex **2** is illustrated in Fig. 4(a) by means of a plot of $\chi_m T$ *vs.* the temperature in the range 300–4.2 K. Upon cooling from room temperature, the $\chi_m T$ product increases very smoothly and continuously increases below 20 K. This indicates that there exists a very weak but unquestionably ferromagnetic coupling between the two Cu^{II} in the dimer. The results are well interpreted on the basis of the Bleaney–Bowers equation.[27] The best fit of the data leads to the parameters $g = 2.04$ and $2J = 1.16$. The reliability factor, defined as $R(\chi_m T) = \Sigma(\chi_m T_{obs} - \chi_m T_{calc})^2/\Sigma(\chi_m T_{obs})^2$, is equal to 4.4×10^{-5}.

There are three types of pyramidal arrangements of chloro-bridged copper(II) dimers in the literature: (I) square pyramids sharing a base-to-apex edge but with parallel basal planes;[28] (II) square pyramids sharing a basal edge with co-planar basal planes;[29] and (III) square pyramids sharing one base-to-apex edge with the two bases nearly perpendicular to one another (only one example until now).[30] The magneto-structural correlations of type I have extensively been studied, and Hatfield and co-workers[31] have shown that the singlet–triplet gap in such complexes varies in a regular way with the quotient φ/R (°/Å), where φ is the bridging angle, Cu^{II}–Cl–Cu^{II}, and R the long, out-of-plane Cu^{II}–Cl bond distance. It was found that for values of this quotient lower than 32.6 and higher than 34.8°/Å the exchange interaction is antiferromagnetic. For values falling between these limits the exchange interaction was ferromagnetic. In the case of our chloro-bridged dimer, $[Cu\mathbf{L^2}Cl]_2[ClO_4]_2$ **2**, the value of the quotient φ/R (°/Å) is 33.4, just falling into the limits, so the ferromagnetic interaction may satisfactorily be understood.

The $\chi_m T$ *vs.* T plot for the phenoxo-bridged dimer $[Cu\mathbf{L^3}(H_2O)]_2[ClO_4]_2$ **3** is given in Fig. 4(b). The singlet–triplet energy gap ($2J$) was deduced from the least-squares fit of the experimental data to temperature for isotropic exchange according to the Bleaney–Bowers equation modified by Kahn to take into account some paramagnetic impurity,[32] eqn. (1). Here ρ is the

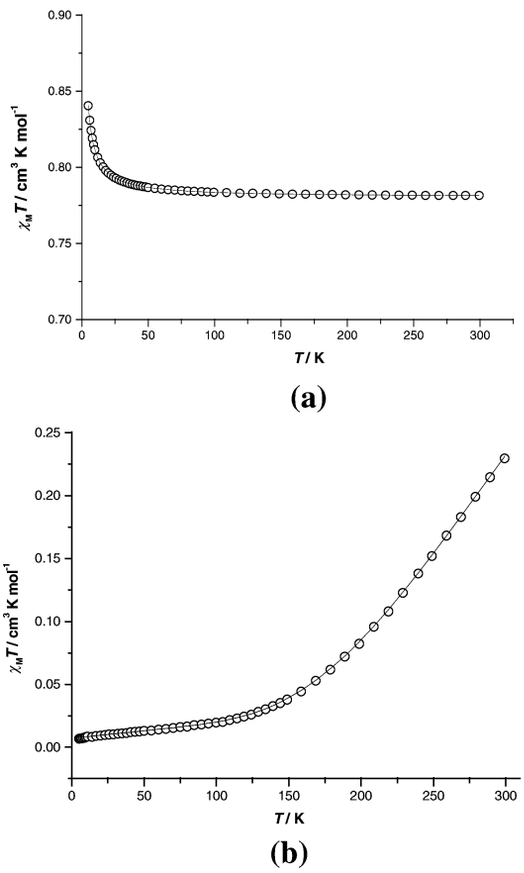

Fig. 4 Magnetic coupling diagrams of (a) the μ-Cl^- bridged binuclear complex **2**, (b) the μ-phenoxo-bridged binuclear complex **3**.

$$\chi_m = (2Ng^2\beta^2/kT)\,[3 + \exp(-2J/kT)]^{-1}\,(1 - \rho) + (Ng^2\beta^2\rho/2kT) + N_\alpha \quad (1)$$

percentage of non-coupled impurity, N_α the temperature-independent paramagnetism, and the other symbols have their usual meanings. In the 300–4.2 K temperature range the $\chi_m T$ value at 299 K is low (0.23 cm^3 K mol^{-1}) and decreases upon cooling. This behavior is characteristic of a large singlet–triplet energy gap and the plateau of $\chi_m T$ below 100 K is due to the proportion of paramagnetic impurity ρ. The best fit, shown as the solid line in Fig. 4(b), afforded the parameter values $2J = -574$ cm^{-1}, $g = 2.19$, $\rho = 0.008$, and $R = 1.2 \times 10^{-5}$ (defined as above).

The magneto-structural correlation of bis-phenoxo-bridged copper(II) dimers has been well studied.[19b] As in the cases of bis-hydroxide- and bis-alkoxide-bridged binuclear copper(II) complexes,[33] the leading factor determining the exchanging interaction is the Cu–O–Cu bridging angle. It has been shown that, for Cu–O–Cu angles ranging from 98.8 to 104.7°, the values of the coupling constant, $-J$, encompass the domain 689–902 cm^{-1}. Assuming a linear correlation between $-J$ and the Cu–O–Cu bridging angle, α, Thompson *et al.*[19b] derived the relationship (2). In **3** the Cu–O–Cu bridging angle is 100.8°, and

$$-J = 31.95\alpha - 2462 \text{ cm}^{-1} \quad (2)$$

the value of J predicted by equation (2) is -758 cm^{-1}, which is a little higher than the experimental datum (-574 cm^{-1}). This difference comes most probably from an effect of the electron-withdrawing substituents bound to the phenolic groups.[34]

Conclusion

Three novel mononuclear and binuclear copper(II) complexes with DACO ligands functionalized by imidazole or phenol pendant(s) have been newly synthesized and characterized, and their structures elucidated by X-ray analyses. A general rule for the coordination modes of the copper(II) complexes with DACO ligands containing different donor pendants has been summarized, which is important for the rational design of functional ligands and complexes with well defined structures and tailored functions, by incorporation of one or two functional donors on the nitrogen atom(s) of such compounds. Furthermore, very different magnetic interactions (from weak ferromagnetic to strong antiferromagnetic) were found to exist in the two binuclear complexes, and the magneto-structural correlations of the chloro- and phenoxo-bridged binuclear copper(II) complexes have been discussed.

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