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Synthesis, crystal structures and properties of copper(II) complexes of Schiff base derivatives containing imidazole and β-alanine groups

La-Sheng Long, Shi-Ping Yang, Ye-Xiang Tong, Zong-Wan Mao, Xiao-Ming Chen* and Liang-Nian Ji

School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou 510275, China. E-mail: cescxm@zsu.edu.cn

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Four copper(II) complexes with Schiff base ligands *N*-[(5-methylimidazol-4-yl)methylene]-β-alanine (HL^1) and *N*-[(1-methylimidazol-2-yl)methylene]-β-alanine (HL^2) and their reduced forms *N*-[(5-methylimidazol-4-yl)methyl]-β-alanine (HL^3) and *N,N*-bis[(5-methylimidazol-4-yl)methyl]-β-alanine (HL^4) have been synthesized. The crystal structures of $[CuL^1(H_2O)(ClO_4)]$ **1**, $[CuL^2(H_2O)(ClO_4)]$ **2**, $[CuL^3(Py)(ClO_4)]$ **3** and $[Cu_2(L^4)_2][ClO_4]_2\cdot 2H_2O$ **4** have been determined. Complexes **1** and **2** are structurally very similar, the copper(II) atom being tridentately chelated by the Schiff base using one carboxy oxygen atom and two nitrogen atoms at the equatorial positions, with the fourth equatorial position being occupied by another carboxy oxygen atom from an adjacent Schiff base; one aqua ligand and one perchlorate oxygen atom ligate at the axial positions, resulting in an elongated octahedral geometry. Each carboxy group in **1** and **2** acts in the *syn-anti* mode and bridges two adjacent copper(II) atoms *via* two equatorial positions, resulting in one-dimensional helical $(Cu–O–C–O–Cu)_n$ chains. In **3** the copper(II) atom is ligated by two nitrogen atoms, one carboxy oxygen atom from an L^3 ligand and another nitrogen atom from pyridine at the equatorial position; the axial positions are occupied by one perchlorato oxygen atom and one carboxy oxygen atom from another L^3 ligand, tridentately chelating an adjacent copper(II) atom, resulting in an elongated octahedral geometry. Complex **4** contains a dimeric cation with two very similar square-pyramidally co-ordinated copper(II) atoms. Each L^4 ligand chelates a copper(II) atom in a tetradentate mode with the three nitrogen atoms occupying the equatorial positions and the carboxy oxygen atom the apical position. The fourth equatorial position is taken by a carboxy oxygen atom from another L^4 ligand chelating another copper(II) atom, resulting in a bis(carboxylato-*O*)-bridged dimeric structure. The electronic and EPR spectra and redox properties of **1**–**4** are also discussed.

Considerable attention has previously been given to Schiff base adducts formed between pyridoxal or its analogues and amino acids.[1,2] Particularly, pyridoxal phosphate (PLP) acts as a cofactor in many enzymes catalysing transformations of amino acids.[3–5] Investigations have been conducted on ternary copper(II) complexes of *N*-salicylideneglycine and its derivatives with imidazole, pyrazole or pyridine by EPR and their redox properties.[6–9] Of particular importance are the chelates containing histidine residues; not only do the polydentate Schiff base ligands provide a useful framework to establish relationships between spectral properties of the complexes and the binding mode of the histidine residue,[10] but also the histidine-like binding modes of amino acid residues may model structural features in biological systems. The investigation of the structures and spectral properties of metal complexes containing histidine[11] or histidyl residues[10,12] is thus very important for elucidating structure/function relations in histidine-containing biological systems. However, the only reported crystal structure containing a histidine Schiff base appears to be a cobalt complex $[Co(SalHis)(Ala)]\cdot 2H_2O$ [SalHis = α-*N*-(*o*-hydroxybenzyl)-L-histidinate, Ala = L-alaninate].[13]

We have recently reported the synthesis, structures and properties of a series of metal complexes with imidazole-containing ligands relevant to structure/function relations of some metalloenzymes.[14] As a sequel, in this paper we report the synthesis of the Schiff base ligands *N*-[(5-methylimidazol-4-yl)methylene]-β-alanine (HL^1), *N*-[(1-methylimidazol-2-yl)methylene]-β-alanine (HL^2) and their reduced forms *N*-[(5-methylimidazol-4-yl)methyl]-β-alanine (HL^3) and *N,N*-bis[(5-methylimidazol-4-yl)methyl]-β-alanine (HL^4), and crystal structures, electronic and EPR spectra and redox properties of their copper(II) complexes, $[CuL^1(H_2O)(ClO_4)]$ **1**, $[CuL^2(H_2O)(ClO_4)]$ **2**, $[CuL^3(Py)(ClO_4)]$ **3** and $[Cu_2(L^4)_2][ClO_4]_2\cdot 2H_2O$ **4**.

Experimental

All reagents were commercially available and used as received. Solvents were dried by conventional procedures prior to use. All samples were thoroughly dried prior to elemental analyses.

Physical measurements

The C, H and N elemental analyses were performed on a Perkin-Elmer 204 elemental analyser. The IR spectra were recorded on a Nicolet 5DX FT-IR spectrophotometer with KBr discs in the 4000–400 cm^{-1} region, electronic spectra on a Shimadzu MPS-200 spectrometer in DMF solutions and X-band EPR spectra from crystalline samples on a Bruker ER-420 spectrometer operating at 77 K in DMF solution. Cyclic voltammetry was performed on an electrochemical analyser in DMF. A platinum wire working electrode, a platinum plate auxiliary electrode and a saturated calomel reference electrode (SCE) were employed.

CAUTION: perchlorate salts of metal complexes are potentially explosive and should be handled in small quantities with care.

Synthesis of ligands

HL^3. To a solution of β-alanine (0.89 g, 10 mmol) in methanol (10 cm^3) containing KOH (0.56 g, 10 mmol) was added

5-methylimidazole-4-carbaldehyde (1.10 g, 10 mmol) in methanol (10 cm^3). The solution was refluxed with stirring for 2 h. The yellowish solution was cooled in an ice-bath, then reduced with an excess of $NaBH_4$ (0.46 g, 12 mmol) in methanol containing a few drops of sodium hydroxide solution. The yellowish colour slowly discharged, and after 10 min the solution was evaporated and extracted with dry methanol, then acidified with HCl gas. The resulting solid was filtered off, washed with dry methanol and diethyl ether, and dried, which yielded 45.6% (Calc. for $C_8H_{13}N_3O_2{\cdot}2HCl$: C, 37.50; H, 5.86; N, 16.41. Found: C, 37.53; H, 6.03; N, 16.34%). IR (KBr, cm^{-1}): 3163m, 3100s, 3071s, 2980s, 2790m, 2600m, 1735s, 1602w, 1539w, 1468m, 1398w, 1370m, 1264m, 1208s, 1159m, 1068m, 1004w, 962w, 871w, 800w, 772m, 695w, 603w, 470w and 435w.

HL^4. To a solution of $HL^3{\cdot}2HCl$ (2.56 g, 10 mmol) in methanol (10 cm^3) containing KOH (1.68 g, 30 mmol) was added 5-methylimidazole-4-carbaldehyde (1.10 g, 10 mmol) in methanol (10 cm^3). The solution was refluxed with stirring for 2 h. The yellowish solution was cooled in an ice-bath, then reduced with an excess of $NaBH_4$ (0.46 g, 12 mmol) in methanol containing a few drops of sodium hydroxide solution. The yellowish colour slowly discharged, and after 10 min the solution was evaporated and extracted with dry methanol, then acidified with HCl gas. The resulting solid was filtered off, washed with dry methanol and diethyl ether, and then dried, which yielded 0.98 g of a solid containing $HL^4{\cdot}4HCl$ (82%) and $HL^3{\cdot}2HCl$ (18%). The percentages of each were calculated according to elemental analysis (Found: C, 36.95; H, 5.76; N, 16.43%).

Preparation of metal complexes

(a) $[CuL^1(H_2O)(ClO_4)]$ 1. To a solution of β-alanine (0.089 g, 1.0 mmol) in methanol (10 cm^3) containing KOH (0.056 g, 1.0 mmol) was added 5-methylimidazole-4-carbaldehyde (0.11 g, 1.0 mmol) in methanol (10 cm^3). The solution was refluxed with stirring for 2 h. To the yellowish solution was added a solution of copper(II) nitrate hydrate (0.20 g, 1.0 mmol) and a solution of sodium perchlorate (0.14 g, 1.0 mmol) in aqueous methanol (10 cm^3, 1:5 v/v). The reaction mixture turned deep blue immediately. After allowing it to stand in air at room temperature for two days, the deposited deep blue crystals of complex **1** were collected and washed with ethanol, yield 67%. A single crystal suitable for X-ray work was obtained by recrystallization in MeCN (Calc. for $C_8H_{12}ClCuN_3O_7$: C, 26.59; H, 3.32; N, 11.63. Found: C, 26.39; H, 3.35; N, 11.54%). IR (cm^{-1}): 3430s, 3128s, 3015s, 2910m, 2853m, 1637s, 1560s, 1518s, 1440m, 1426m, 1398m, 1349w, 1293w, 1236w, 1215w, 1124s, 1089s, 1075s, 976w, 878w, 765w, 695w and 632s.

(b) $[CuL^2(H_2O)(ClO_4)]$ 2. Complex **2** was prepared as for **1**. Deep blue needle crystals were obtained, yield 65% (Calc. for $C_8H_{12}ClCuN_3O_7$: C, 26.59; H, 3.32; N, 11.63. Found: C, 26.35; H, 3.28; N, 11.61%). IR (cm^{-1}): 3655s, 3325s, 3142s, 3029s, 2910m, 2853m, 1637s, 1567s, 1518s, 1454m, 1426s, 1356w, 1293w, 1250w, 1215w, 1145s, 1110s, 1075s, 962w, 828w, 765w, 674w and 632s.

(c) $[CuL^3(Py)(ClO_4)]$ 3. To an ethanol (10 cm^3) solution of $L^3{\cdot}2HCl$ (0.256 g, 1.0 mmol) containing KOH (0.17 g, 3.0 mmol) and pyridine (0.079 g, 1.0 mmol), an aqueous ethanol (10 cm^3, 50% v/v) solution of copper(II) nitrate hydrate (0.20 g, 1.0 mmol) and $NaClO_4{\cdot}H_2O$ (0.14 g, 1.0 mmol) was added dropwise while stirring. After filtration, the deep blue solution was allowed to stand at room temperature in air, yielding transparent deep blue polyhedral crystals of complex **3**, yield 57% (Calc. for $C_{13}H_{17}ClCuN_4O_6$: C, 36.80; H, 4.01; N, 13.20. Found: C, 36.39; H, 3.95; N, 13.54%). IR (cm^{-1}): 3571s, 3458s, 3148s, 3043s, 2903m, 2714m, 1630s, 1581s, 1525s, 1447m, 1426m, 1384m, 1328w, 1278w, 1243w, 1138s, 1117s, 1082s, 990w, 878w, 821w, 667w and 632s.

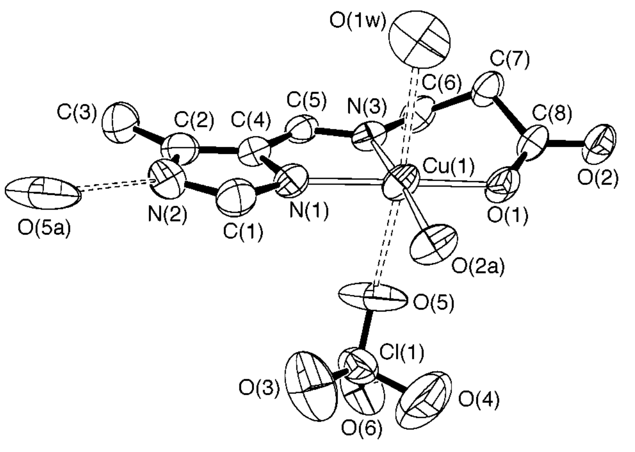

Fig. 1 An ORTEP view of the co-ordination geometry and hydrogen bonding scheme in complex **1**.

(d) $[Cu_2(L^4)_2][ClO_4]_2{\cdot}2H_2O$ 4. To an ethanol (10 cm^3) solution of $L^4{\cdot}4HCl$ (0.423 g, 1.0 mmol) containing NaOH (0.20 g, 5.0 mmol), an aqueous ethanol (10 cm^3, 50% v/v) solution of copper(II) nitrate hydrate (0.20 g, 1.0 mmol) and $NaClO_4{\cdot}H_2O$ (0.14 g, 1.0 mmol) was added dropwise while stirring. After filtration, the blue solution was allowed to stand at room temperature in air, yielding transparent deep blue polyhedral crystals of complex **4**, yield 35% (Calc. for $C_{13}H_{20}ClCuN_5O_7$: C, 34.14; H, 4.38; N, 15.32. Found: C, 34.39; H, 4.35; N, 15.54%). IR (cm^{-1}): 3655s, 3325s, 3142s, 3029s, 2910m, 2853m, 1560s, 1518s, 1454m, 1426s, 1356w, 1293w, 1250w, 1215w, 1145s, 1110s, 1075s, 962w, 828w, 765w, 674w and 632s.

X-Ray crystallography

Diffraction intensities for the four complexes were collected at 293 K on a Siemens R3m diffractometer. Lorentz-polarization and absorption corrections were applied. The structure solution and full-matrix least-squares refinement based on F^2 were performed with the SHELXS 97 and SHELXL 97 program packages, respectively.[15,16] Complex **2** crystallizes in a non-centrosymmetric space group; the absolute structure has been determined with a Flack parameter of 0.10(6).[17] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the organic ligands were generated geometrically (C–H 0.96 Å) and those of the aqua ligands located from the difference maps; all the hydrogen atoms were assigned the same isotropic thermal parameters and included in the structure-factor calculations. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections incorporated.[18] The crystallographic data for **1**–**4** are summarized in Table 1. Selected bond distances and angles are given in Table 2.

CCDC reference number 186/1439.

See http://www.rsc.org/suppdata/dt/1999/1999/for crystallographic files in .cif format.

Results and discussion

Crystal structures

(a) $[CuL^1(H_2O)(ClO_4)]$ 1. An ORTEP[19] view of the co-ordination environment of complex **1** is shown in Fig. 1. The surrounding of each copper(II) atom is (4+2). The L^1 ligand acts in a tridentate chelate mode for the copper(II) atom, utilizing the two nitrogen atoms and one carboxy oxygen atom to bind the metal atom at the equatorial positions; the fourth equatorial position is occupied by an oxygen atom O(2a)

Table 1 Crystal data and structure refinement for complexes **1**–**4**

	1	**2**	**3**	**4**
Empirical formula	$C_8H_{12}ClCuN_3O_7$	$C_8H_{12}ClCuN_3O_7$	$C_{13}H_{17}ClCuN_4O_6$	$C_{26}H_{40}Cl_2Cu_2N_{10}O_{14}$
Formula weight	361.20	361.20	424.29	914.66
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*Pna*2$_1$	*P*2$_1$/*n*	*P*2$_1$/*c*
a/Å	14.916(7)	12.793(10)	10.314(12)	8.240(3)
b/Å	7.458(4)	13.167(8)	8.167(4)	18.185(5)
c/Å	23.687(12)	7.731(3)	19.468(16)	23.445(6)
β/°	97.89		102.09	90.96(3)
Z	4	4	4	4
V/Å^3	2610(2)	1302.3(8)	1604(2)	3512.6(18)
μ(Mo-Kα)/cm^{-1}	1.914	1.918	1.569	1.445
*R*1 ($I > 2\sigma$)	0.0728	0.0618	0.0566	0.0559
*R*2 (all data)	0.2041	0.1858	0.1508	0.1367

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1**–**4**

1			
Cu(1)–O(1)	1.913(5)	Cu(1)–N(1)	1.937(6)
Cu(1)–O(2a)	1.953(5)	Cu(1)–N(3)	1.967(5)
N(3)–C(6)	1.443(13)	C(4)–C(5)	1.424(8)
N(3)–C(5)	1.263(8)		
Cu(1)$\cdots$O(1w)	2.624(8)	Cu(1)$\cdots$O(5)	2.701(8)
N(2)$\cdots$O(5b)	2.976(1)		
C(5)–N(3)–C(6)	122.3(6)	C(5)–N(3)–Cu(1)	114.2(5)
C(6)–N(3)–Cu(1)	123.5(4)		
2			
Cu(1)–O(2a)	1.933(4)	Cu(1)–N(1)	1.937(6)
Cu(1)–O(1)	1.941(5)	Cu(1)–N(3)	2.025(5)
Cu(1)$\cdots$O(1w)	2.489(6)	Cu(1)$\cdots$O(3)	2.749(10)
N(3)–C(5)	1.278(9)	N(3)–C(6)	1.408(10)
O(2)–Cu(1b)	1.933(4)	C(4)–C(5)	1.385(10)
C(5)–N(3)–C(6)	123.7(5)	C(5)–N(3)–Cu(1)	111.2(5)
C(6)–N(3)–Cu(1)	125.2(4)		
3			
Cu(1)–O(1)	1.916(4)	Cu(1)–N(1)	1.952(4)
Cu(1)–N(3)	1.991(5)	Cu(1)–N(4)	2.001(5)
N(3)–C(5)	1.455(6)	C(4)–C(5)	1.492(7)
N(3)–C(6)	1.453(6)		
Cu(1)–O(2a)	2.722(4)	Cu(1)–O(5)	2.795(6)
N(2)–O(2b)	2.758(6)		
C(5)–N(3)–C(6)	113.8(4)	C(6)–N(3)–Cu(1)	117.5(3)
C(5)–N(3)–Cu(1)	111.2(3)		
4			
Cu(1)–N(4)	1.935(4)	Cu(1)–N(1)	1.937(4)
Cu(1)–O(3)	1.949(4)	Cu(1)–N(3)	2.081(4)
Cu(1)–O(1)	2.263(4)	Cu(1)–Cu(2)	3.2557(15)
Cu(2)–N(6)	1.931(4)	Cu(2)–N(9)	1.940(4)
Cu(2)–O(1)	1.955(3)	Cu(2)–N(8)	2.077(4)
Cu(2)–O(3)	2.259(4)	N(3)–C(6)	1.489(7)
N(2)–O(11)	3.054(8)	N(3)–C(11)	1.497(7)
N(3)–C(5)	1.495(7)	C(4)–C(5)	1.488(8)
N(5)–O(2w)	2.763(7)	N(8)–C(31)	1.479(7)
N(8)–C(26)	1.492(7)	N(8)–C(25)	1.493(7)
N(7)–O(1w)	2.729(6)	O(1w)–O(2a)	2.734(6)
N(10)–O(8)	2.862(7)	N(2)–O(12)	2.979(7)
O(2w)–O(4b)	2.786(6)		
C(5)–N(3)–C(6)	109.5(5)	C(6)–N(3)–Cu(1)	111.2(5)
C(5)–N(3)–Cu(1)	106.6(3)	C(5)–N(3)–C(11)	107.6(4)

Symmetry codes: for **1**, a, $-x + 3/2, y - 1/2, -z + 1/2$; b, $x, y - 1, z$; c, $-x + 3/2, y + 1/2, -z + 1/2$; for **2**, a, $-x, -y + 1, z - 1/2$; b, $-x, -y + 1, z + 1/2$; for **3**, a, $-x + 3/2, y + 1/2, -z + 3/2$; b, $x - 1/2, -y + 1/2, z - 1/2$; for **4**, a, $-x + 1, y + 1/2, -z + 1/2$; b, $-x, -y, -z$.

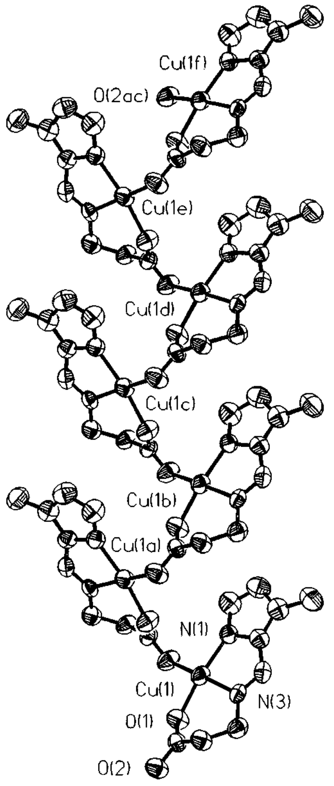

Fig. 2 An ORTEP view of the helical chain of complex **1** running along the *a* axis.

belonging to the carboxy group of an adjacent and symmetry-related fragment. The bond lengths Cu(1)–N(1) and Cu(1)–N(3) are 1.937(6) and 1.967(5) Å, respectively; the Cu–O (carboxy) distances are 1.913(5) and 1.953(5) Å. An aqua ligand and a perchlorate oxygen atom ligate the copper(II) atom at the axial positions with much longer bond distances [Cu(1)–O(1w) 2.624(8), Cu(1)–O(5) 2.701(8) Å], resulting in an elongated octahedral geometry.

It is interesting that each carboxylate group acts in the bidentate *syn-anti* mode and bridges each pair of adjacent copper(II) atoms (C$\cdots$Cu 4.757 Å) *via* the two equatorial positions, giving rise to one-dimensional (Cu–O–C–O–Cu)$_n$ skeletons running parallel to the crystallographic *a* axis (Fig. 2), which may best be visualized as helix-like chains, being similar to an example previously documented.[20]

(b) [CuL^2(H$_2$O)(ClO$_4$)] 2. An ORTEP[19] view of the co-ordination environment of complex **2** is shown in Fig. 3. The crystal structure of **2** is very similar to that of **1**. The bond lengths Cu(1)–N(1) and Cu(1)–N(3) are 1.937(6) and 2.025(5) Å, and Cu(1)–O(1) and Cu(1)–O(2a) are 1.941(4) and 1.933(4) Å, respectively. The differences of the corresponding values of the co-ordination bonds between **1** and **2** may be attributed to the difference in the imidazole groups in L^1 and L^2, where the

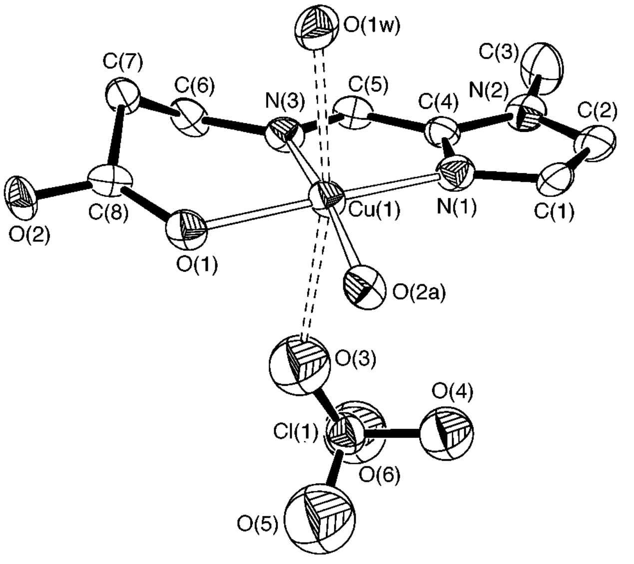

Fig. 3 An ORTEP view of the co-ordination geometry and hydrogen bonding scheme in complex **2**.

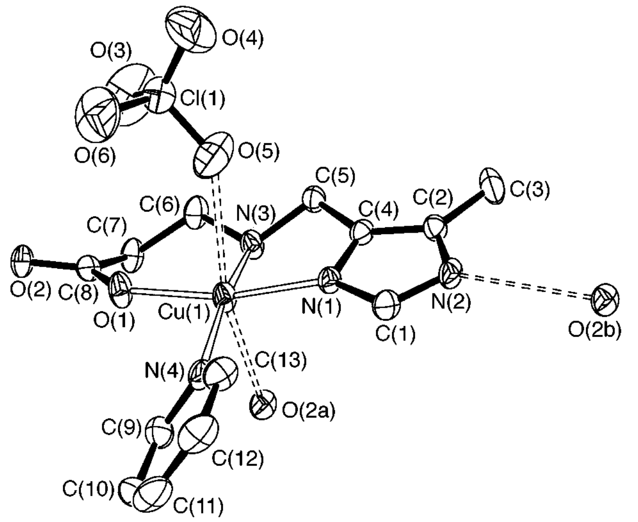

Fig. 4 An ORTEP view of the co-ordination geometry and hydrogen bonding scheme in complex **3**.

imidazole group in L^1 is hydrogen bonded to a perchlorate group and that in L^2 is methylated; this may result in different co-ordination abilities for the two organic ligands.[21,22]

Also similar to that of complex **1**, each carboxylate group acts in a bidentate *syn-anti* mode and bridges each pair of adjacent copper atoms (Cu···Cu 4.867 Å) *via* the two equatorial positions, giving rise to one-dimensional $(Cu–O–C–O–Cu)_n$ helix-like chains in the solid.

(c) [CuL^3(Py)(ClO$_4$)] 3. An ORTEP[19] view of the molecular structure of complex **3** is shown in Fig. 4. The crystal structure consists primarily of discrete molecules of **3** with the copper(II) atom in a distorted square-planar geometry. The metal atom is tridentately chelated by an L^3 ligand and the co-ordination sphere is completed by a pyridine ligand. One perchlorate oxygen atom and a carboxy oxygen atom from an adjacent molecule have weak interaction with the metal through the axial positions [Cu(1)···O(5) 2.795(6), Cu(1)···O(2a) 2.722(4) Å]. The significantly weaker axial interaction of the copper(II) atom may be attributed to the stronger donor ability of pyridine in **3**, in comparison to that of a carboxy group in **1** and **2**.

The copper(II)–imidazole Cu(1)–N(1) bond [1.952(4) Å] is slightly shorter than that of the copper(II)–pyridine Cu(1)–N(4) bond [2.001(5) Å] and that of the copper(II)–amine Cu(1)–N(3) bond [1.991(5) Å]. The successful *in situ* reduction of the imine group is evident from the N(3)–C(5) distance [1.455(6) Å] compared with those [1.263(8) and 1.278(9) Å] for the related ligand (L^1 and L^2) in **1** and **2**. Furthermore, the bond length C(4)–C(5) [1.492(7) Å] is typical of a single bond, which is significantly longer than the corresponding bonds in **1** and **2** [1.424(8) and 1.385(10) Å], and indicates the loss of conjugation.[23] The bond angles centred about the N(3) atom are 113.8(4), 117.5(3) and 111.2(3)° for C(5)–N(3)–C(6), C(6)–N(3)–Cu(1) and C(5)–N(3)–Cu(1), respectively, being consistent with a sp^3 tetrahedral configuration, and similar to those for [Co(SalHis)(Ala)].[13]

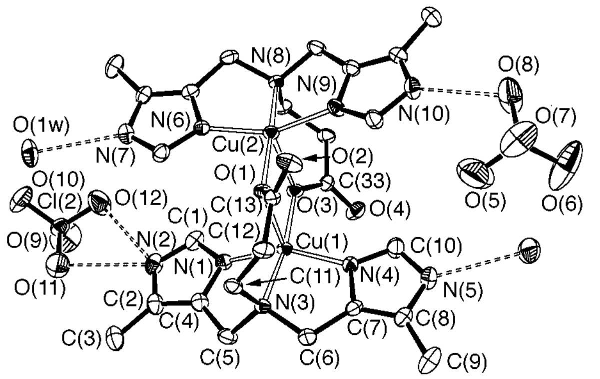

Fig. 5 An ORTEP view of the co-ordination geometry and hydrogen bonding scheme in complex **4**.

(d) [Cu$_2$(L^4)$_2$][ClO$_4$]$_2$·2H$_2$O 4. The crystal structure of complex **4** consists of discrete carboxylate-bridged dimeric cations, perchlorate anions and lattice water molecules. An ORTEP[19] view of the dimeric cation is shown in Fig. 5, in which the two crystallographically independent copper(II) atoms are in very similar co-ordination environments. The anionic L^4 ligand chelates a square-pyramidally co-ordinated copper(II) atom in a tetradentate fashion with the three nitrogen atoms occupying the equatorial positions and the carboxy oxygen atom occupying the apical position. The fourth equatorial position is taken by a carboxy oxygen atom from another L^4 ligand chelating another copper(II) atom in the dimeric cation. The bond lengths Cu(1)–N(1), Cu(1)–N(3) and Cu(1)–N(4) are 1.937(4), 2.081(4) and 1.935(4) Å, respectively, while Cu(2)–N(6), Cu(2)–N(8) and Cu(2)–N(9) are 1.931(4), 2.077(4) and 1.940(4) Å, respectively. The two C–O distances of each carboxylate group are markedly different [1.264(6) and 1.216(7); 1.270(6) and 1.213(7) Å], due to the monodentate μ-carboxylate-*O* bridging mode, and similar to those documented for some bis(carboxylato)-dicopper(II) complexes.[24] The intradimeric Cu(1)···Cu(2) distance [3.256(2) Å], mainly dominated by the nature and co-ordination mode of the bridging groups,[24,25] is shorter than those found in related dinuclear copper(II) complexes (average Cu···Cu 3.4 Å).[25] The bond lengths Cu(1)–O(1) [2.263(4) Å] and Cu(2)–O(3) [2.259(4) Å] are significantly longer than Cu(2)–O(1) [1.955(3) Å] and Cu(1)–O(3) [1.949(4) Å], respectively, which is due to the Jahn–Teller-distorted copper(II).[26]

Similar to complex **3**, the reduction of the imine group in **4** is also evident from the bond lengths of N(3)–C and N(8)–C [1.479(7) to 1.497(7) Å]. The bond angles centred about the N(3) atom are 109.5(5), 111.2(5), 106.6(3) and 107.6(4)° for C(6)–N(3)–C(5), C(6)–N(3)–Cu(1), C(5)–N(3)–Cu(1) and C(5)–N(3)–C(11), respectively, which are consistent with a sp^3 tetrahedral configuration and show smaller deviations from the idealized geometry.

Electronic and EPR spectra

The electronic spectral data of the four complexes are listed in Table 3. The UV spectra exhibit an intense absorption band

Table 3 Electronic and EPR data of complexes **1**–**4**

	Electronic spectra (nm)		EPR data		
Complex	d–d	$\pi^* \longleftarrow \pi$	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$/G
1	670.1	299.7	2.307	2.031	180.5
2	688.5	332.9	2.331	2.034	183.5
3	666.5	279.1	2.291	2.042	177.5
4	668.3	272.7	2.301	2.031	g 4.2

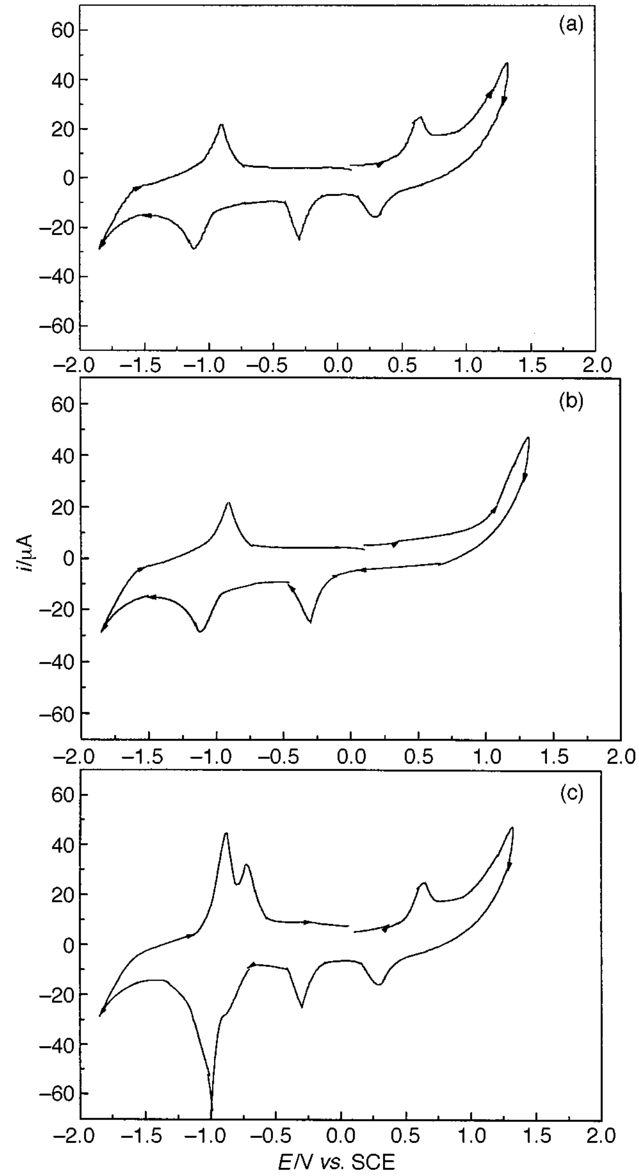

Fig. 6 Cyclic voltammograms for complexes (a) **1**, (b) **2** and (c) **4** in DMF at room temperature with 0.1 mol L^{-1} $Bu^n{}_4NPF_6$ as electrolyte at platinum electrode and SCE reference electrode. Conditions: 1.0 × 10^{-4} mol L^{-1}, $v = 100$ mV s^{-1}.

at 270–300 nm in DMF solution, which can be attributed to a $\pi^* \longleftarrow \pi$ transition of the conjugated imine chromophore. The complexes exhibit additional weaker and approximately symmetrical absorption bands in visible region at 660–690 nm, which are assigned to d–d transitions.[27] It is important to note that the violet shift of the $\pi^* \longleftarrow \pi$ transition for **3** and **4** in comparison to those for **1** and **2** indicates that the imine groups have been reduced, and reinforces this assignment; these observations are consistent with those found for copper(II) complexes with unreduced and reduced Schiff bases condensed with salicylaldehyde and glycine.[23] In contrast to the copper(II) complex of the Schiff base derived from 2-formylpyridine and histidine, we did not observe decomposition of **1** and **2**.[6]

The EPR spectra recorded on microcrystalline samples at 77 K in DMF solution show axial spectra for complexes **1**–**3** (Table 3), indicating that **1**, **2** and **3** were deaggragated in solution and the copper(II) atom adopts elongated octahedral or square-planar co-ordination geometry in DMF solution.[28] For **4** the EPR spectrum shows an axial spectrum with $g_{\parallel} = 2.301$ and $g_{\perp} = 2.024$ and a very weak half-field resonance with $g = 4.2$ under the same conditions, indicating that **4** remains dimeric in solution.

Electrochemistry

Complexes **1**, **2** and **4** underwent an overall cyclic voltammetric process in DMF containing 0.1 mol L^{-1} of $Bu^n{}_4NPF_6$ in the range 2.0 to −2.0 V at room temperature starting with oxidation as shown in Fig. 6. Cyclic voltammetry of **1** displays one reversible wave, one irreversible wave and one quasi-reversible wave. The quasi-reversible redox couple occurs with the oxidation peak at +0.68 V and the corresponding reduction peak at +0.31 V, which may be assigned to the imidazole group of a ligand-based redox couple. The irreversible redox couple occurs with the reduction peak at −0.28 V is assigned to the reaction $[Cu^{II}L^1]^+ + e \longrightarrow [Cu^{I}L^1]^+$ by comparison with the reduction potential value (−0.27 V *vs.* SCE) of Cu^{II}–Cu^{I}.[29] The reversible redox couple (reduction peak at −1.05 V) may be assigned to the imine group of the L^1 ligand. Complex **2** exhibits one reversible wave and one irreversible wave [Fig. 6(b)], which supports the assignment of the quasi-reversible redox couple in **1** for the redox of the imidazole group in L^1 since **2** does not show a similar quasi-reversible wave in the redox process. Similar to **1**, the irreversible and reversible redox couples in **2** were assigned to the reaction $[Cu^{II}L^2]^+ + e \longrightarrow [Cu^{I}L^2]^+$ and the imine group of L^2, respectively. Cyclic voltammetry of **4** displays two reversible waves, one irreversible and one quasi-reversible. The quasi-reversible redox couple occurs with the oxidation peak at +0.66 V and the corresponding reduction peak at +0.30 V, which is assigned to a ligand-based redox couple. The irreversible redox couple occurs with the reduction peak at −0.28 V and is assigned to the reaction $[Cu^{II}{}_2(L^4)_2]^{2+} + e \longrightarrow [Cu^{I}Cu^{II}(L^4)_2]^{2+}$. The reversible redox couple occurs with the reduction peak at −0.85 V and the corresponding oxidation peak at −0.75 V is a single-electron process, which may be assigned to the reaction $[Cu^{I}Cu^{II}(L^4)_2]^{2+} + e \rightleftharpoons [Cu^{I}{}_2(L^4)_2]^{2+}$. The reversible redox couple occurs at −1.02/−0.90 V and may be assigned to a redox process of L^4. These observations suggest that ligands L^1, L^2 and L^4 can stabilize the copper(I) ions in the complexes due to the imidazole groups forming π back bonding with the copper(I) atoms.

Conclusion

The Schiff base ligands containing an imidazole group and β-alanine and imine-reduced ligands bonding copper(II) have yielded complexes with tri- or tetra-dentate co-ordination modes. The EPR spectra indicate that **1**, **2** and **3** were deaggragated in DMF solution, while **4** remains dimeric. The cyclic voltammograms of **1**, **2** and **4** indicate that ligands L^1, L^2 and L^4 can stabilize the copper(I) ions in the complexes due to the imidazole groups forming π back bonding with the copper(I) atoms.

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