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Coordination chemistry of copper(II) with oxaaza macrocyclic ligands. Crystal structure of a dinuclear tetramer copper(II) complex

Carlos Lodeiro, Rufina Bastida *, Emilia Bertolo, Alejandro Macías, Adolfo Rodríguez

Departamento de Química Inorgánica, Universidad de Santiago de Compostela, Avda. das Ciencias s/n, 15782 Santiago de Compostela, Spain

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Abstract

A new series of copper(II) nitrate and perchlorate complexes with eight different oxaaza macrocyclic ligands (L^1–L^8) have been prepared and characterised. Complexes with the diiminic ligands L^1–L^6 have been obtained by template condensation of the appropriate dialdehyde and diamine precursors; the reduced L^7 and L^8 macrocycles have been synthesised using a direct route. The overall geometry and bonding mode have been deduced on the basis of elemental analysis data, IR, FAB, UV–Vis spectroscopy, cyclic voltammetry, and conductivity and magnetic susceptibility measurements. After treatment of an acetonitrile solution of the complex $[L^6Cu](ClO_4)_2 \cdot 5H_2O$ with acetic acid 15%, dark blue single crystals, the result of a secondary reaction, were isolated and characterised as a new binuclear tetramer copper(II) complex, with formula $C_{13}H_{28}ClCu_2N_3O_{10}$.

Keywords: Copper complexes; Template synthesis; Direct synthesis; Schiff-base; Oxaaza macrocycles

1. Introduction

Since the late 1980s, the study of mono- and dinuclear copper(II) complexes has attracted considerable attention, due to the relevance of Cu^{2+} in biological systems [1]. There have been several attempts to model the active centre of biological molecules that include two metal copper atoms on their structure, such as haemocyanin or other biological proteins [2–6]. Polynuclear copper complexes derived from open ligands have also been prepared, in order to investigate their physical and physicochemical properties [7].

In the field of macrocycles, different approaches have been chosen [8,9]. Macrocycles with a large cavity, which allow accommodating two metal ions, can be used to hold the metal centre at a fixed distance [10–13]. In these systems, there is often an additional internal or external bridging group, which completes the structures of the binuclear species; this has the advantage of being relatively rigid and thus give structurally well defined moieties [14–16].

We report herein an study of the complexation capability of Cu(II) towards eight different oxaaza macrocyclic ligands derived from 2,6-bis(2-formylphenoxymethyl)pyridine (L^1, L^3, L^4, L^6, L^7) or 1,7-bis(2′-formylphenyl)-1,4,7-trioxaheptane (L^2, L^5, L^8) and the appropriate aliphatic or aromatic diamine precursor. The complexes with the Schiff-base macrocycles L^1–L^6 have been synthesised using Cu(II) as template agent; the complexes with reduced macrocycles L^7 and L^8 have been obtained by direct reaction between the corresponding preformed macrocycle and the metal ion. Several mononuclear or dinuclear complexes have been obtained using the two aforementioned methods. Transmetallation reaction of the La(III) perchlorate complex with L^1, in the presence of $Cu(ClO_4)_2$, yielded the corresponding dinuclear copper(II) complex with L^1. Finally, a new tetranuclear structure, a secondary product obtained by recrystallisation of the Cu(II) perchlorate complex with L^6 in acidic media, is also reported Fig. 1.

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* Corresponding author. Tel.: +34-981-591076; fax: +34-981-597525.

E-mail address: qibastid@uscmail.usc.es (R. Bastida).

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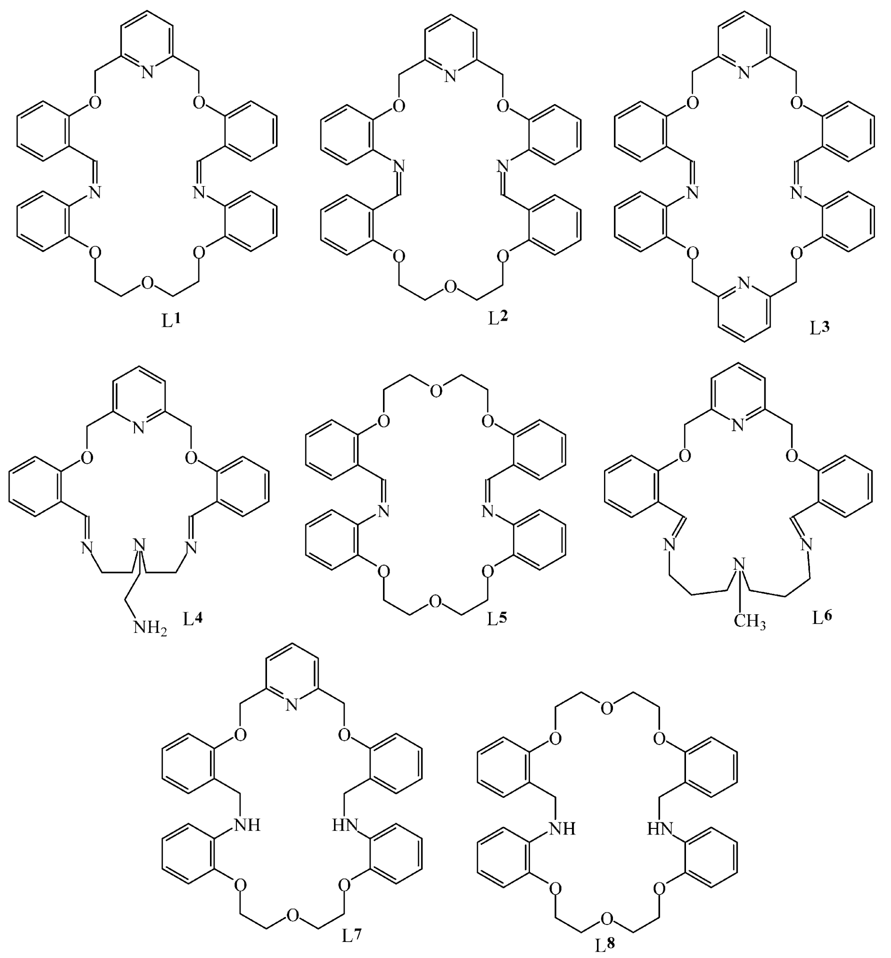

Fig. 1. Macrocyclic ligands L^1–L^8 $\mathbf{L^1}$ = 3, 18, 21, 24, 39-pentaoxa-11, 31, 45-triazahexacyclo[39·3·1·$O^{4,9}$·$O^{12,17}$·$O^{25,30}$·$O^{38,39}$] pentatetraconta-1, 4(9), 5, 7, 10, 12(17), 13, 15, 25(30), 26, 28, 31, 33(38), 34, 36, 41(45), 42-heptadecaene. $\mathbf{L^2}$ = 3, 18, 21, 24, 39-pentaoxa-10, 32, 45-triazahexacyclo[39·3·1·$O^{4,9}$·$O^{12,17}$·$O^{25,30}$·$O^{38,39}$] pentatetraconta-1, 4(9), 5, 7, 10, 12(17), 13, 15, 25(30), 26, 28, 31, 33(38), 34, 36, 41(45), 42-heptadecaene. $\mathbf{L^3}$ = 3, 18, 26, 41-tetraoxa-10, 34, 47, 48-tetraazaheptacyclo [41·3·1·$1^{20,24}$·$O^{4,9}$·$O^{12,17}$·$O^{27,32}$·$O^{35,40}$] octatetraconta-1(47), 4(9), 5, 7, 10, 12(17), 13, 15, 20, 22, 24(48), 27(32), 28, 30, 33, 35, 37, 39, 43, 45-icosaene. $\mathbf{L^4}$ = 2-[3, 25-dioxa-11, 14, 17, 31 -tetrazatetracyclo[25·3·1·$O^{4,9}$·$O^{19,24}$] hentriaconta-1(31), 4(9), 5, 7, 10, 17, 19(24), 20, 22, 27, 29-undecaen-14-yl]-1-ethanamine. $\mathbf{L^5}$ = 12, 13, 15, 16, 29, 30, 32, 33-octahydrotetrabenzo [h, l, u, y][1, 4, 7, 14, 17, 20, 10, 24] hexaoxadiazacyclohexacosine. $\mathbf{L^6}$ = 15-methyl-3, 27-dioxa-11, 15, 19, 33-tetraazatetracyclo [27·3·1·$O^{4,9}$·$O^{21,26}$]-tritiaconta-1(32), 4(9), 5, 7, 10, 19, 21(26), 22, 24, 29(33), 30-undecane. $\mathbf{L^7}$ = 3, 18, 21, 24, 39-pentaoxa-11, 32, 45-triazahexacyclo[39·3·1·$O^{4,9}$·$O^{12,17}$·$O^{25,30}$·$O^{38,39}$] pentatetraconta-1, 4(9), 5, 7, 10, 12(17), 13, 15, 25(30), 26, 28, 31, 33(38), 34, 36, 41(45), 42-pentadecaene. $\mathbf{L^8}$ = 5, 6, 12, 13, 15, 16, 22, 23, 29, 30, 32, 33-dodecahydrotetrabenzo [h, l, u, y][1, 4, 7, 14, 17, 20, 10, 24] hexaoxadiazacyclo hexacosine.

2. Experimental

2.1. Measurements

Elemental analyses were carried out by the University of Santiago de Compostela Microanalitycal Service on Carlo Erba 1108 and Leco CNHS-932 microanalysers. Infrared spectra were recorded as KBr discs using a Mattson Cygnus 100 spectrophotometer. Positive-ion FAB mass spectra were recorded on a Kratos MS50TC spectrometer using a 3-nitrobenzyl alcohol (MNBA) matrix. Conductivity measurements were carried out in 10^{-3} mol dm^{-3} acetonitrile solutions at 25 °C using a WTW LF-3 conductivimeter. The electronic absorption spectra of complexes (CH_3CN solutions) were measured in the range 220–900 nm using a Perkin–Elmer Lambda 6 spectrophotometer. Cyclic voltammetry experiments were performed using an EG&G PAR potentiostat/galvanostat, model 273. The working and reference electrodes were glassy carbon and Pt in CH_3CN. Solutions containing 10^{-3} M of the respective complex and 0.1 M TEAP (Et_4NClO_4) were placed in a cell and pure Ar(g) and N_2, pre-saturated with solvents was passed through the solution during the experiment. The magnetic susceptibility was run on a Superconducting Quantum Interferometer Device working at room temperature.

2.1.1. Crystal structure data and determination

A dark blue crystal of $[CuL^9(CH_3COO)Cu(CH_3COO)_2]ClO_4$, $L^9 = NH_2(CH_2)_3NHCH_3(CH_2)_3NH_2$ crystallised from acetonitrile/diethyl ether/chloroform was used for the structure determination. The chosen crystal was mounted on a glass fiber using an epoxy resin. Data was collected at 293 K Siemens CCD SMART area detector single crystal diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) by the ω scan method. 11 565 reflections measured, all of which were corrected for Lorentz and polarisation effects and for absorption [17]. The structure was solved by direct methods followed by Fourier-difference syntheses and refined by full-matrix least-squares methods on F^2. The amine hydrogen atoms were located on a Fourier map. All other hydrogen atoms were included in calculated positions and refined in riding mode with $U(H)$ equal to 1.2 times U_{eq} of the parent atom. A summary of the experimental and structure solution procedure is given in Table 2.

Data collection and cell refinement: Siemens SMART [18]. Data reduction: Siemens SAINT [19]. Program(s) used to solve and refine structures: SHELX-97 [20]. Molecular graphics: ORTEP-3 [21]. Software used to prepare material for publication: SHELX-97.

2.1.2. Chemicals and starting materials

2,6-Bis(2-formylphenoxymethyl)pyridine and 1,7-bis(2′-formylphenyl)-1,4,7-trioxaheptane were prepared according to the literature method [22–24]. 1,5-Bis(2-aminophenoxy)-3-oxapentane and 2,6-bis(*o*-aminophenoxymethyl)pyridine were prepared by reduction of the corresponding dinitro precursors using a similar procedure to that described previously [25–28]. Tris(2-aminoethyl)amine and *N*,*N*-bis(3-aminopropyl)methylamine, and nitrate and perchlorate copper salts were commercial products (from Alfa and Aldrich) used without further purification. Solvents were of reagent grade purified by the usual methods.

Table 1
^{1}H NMR and ^{13}C NMR data of L^6 in $CDCl_3$

Assignment	Shift (ppm), integration	Assignment	Shift (ppm)
Ha	7.73(t), 1*H*	C_1	137.8
Hb	7.95(d), 2*H*	$C_2=C_{28}$	127.6
Hc	5.30(s), 4*H*	$C_3=C_{27}$	125.1
Hd	6.85(d), 2*H*	$C_4=C_{26}$	28.63
He	6.81(t), 2*H*	$C_5=C_{25}$	156.7
Hf	7.30(t), 2*H*	$C_6=C_{24}$	131.7
Hg	7.40(d), 2*H*	$C_7=C_{23}$	112.4
Hh	8.80(s), 2*H*	$C_8=C_{22}$	121.4
Hi	3.63(t), 4*H*	$C_9=C_{21}$	120.1
Hj	1.85(t), 4*H*	$C_{10}=C_{20}$	157.3
Hk	2.45(t), 4*H*	$C_{11}=C_{19}$	156.7
Hm	2.22(s), 3*H*	$C_{12}=C_{18}$	60.1
		$C_{13}=C_{17}$	28.6
		$C_{14}=C_{16}$	55.5
		C_{15}	42.3

s, Singlet; d, doublet; t, triplet.

Caution: Although no problems were encountered during the course of this work, attention is drawn to the potentially explosive nature of perchlorates.

The synthesis of the free macrocyclic ligands L^1–L^3, L^5, L^7–L^8 has already been described in previous papers [29–31].

2.2. Synthesis of the Schiff-base macrocycles L^4 and L^6

A solution of the corresponding diamine precursor (2 mmol) (tris(2-aminoethyl)amine for L^4 and *N*,*N*-bis(3-aminopropyl)methylamine for L^6) in hot solvent (MeOH for L^4 and Abs. EtOH for L^6, 50 cm^3) was added dropwise to a refluxing solution of 2,6-bis(2-formylphenoxymethyl)pyridine (2 mmol) in the same hot solvent (50 cm^3). The resulting solution was gently refluxed with magnetic stirring for ca. 8 h for L^4 and 5 h for L^6. The colour changed to yellow in both the cases. The solution was allowed to cool and then concentrated in a rotary evaporator. An orange–yellow powder precipitated, and it was filtered off, washed with cold diethyl ether and dried in vacuo.

2.2.1. L^4

Yield 78%. (Found: C, 58.90; H, 7.75; N, 13.15. $C_{27}H_{31}N_5O_2 \cdot 5H_2O$ requires C, 59.25; H, 7.55; N, 12.80%); m.p. 250–260 °C (unstable); IR (KBr disc): $\nu(NH_2)$ 3064 cm^{-1}, $\nu(C{=}N)_{imi}$ 1662 cm^{-1}, $\nu(C{=}C)$ and $\nu(C{=}N)$ 1596 cm^{-1}. Mass spectrum (positive-ion FAB): m/z 457 $[L^4+H]^+$.

The ligand is air stable, slightly soluble in dichloromethane, and insoluble in acetonitrile, absolute ethanol, chloroform, dimethylformamide, dimethyl sulfoxide, diethyl ether, and water.

2.2.2. L^6

Yield 65%. (Found: C, 63.30; H, 7.05; N, 9.90. $C_{28}H_{32}N_4O_2 \cdot 4H_2O$ requires C, 63.60; H, 7.63; N, 10.55%); m.p. 185–190 °C; IR (KBr disc): $\nu(C{=}N)_{imi}$ 1636 cm^{-1}, $\nu(C{=}C)$ and $\nu(C{=}N)$ 1596, 1449 cm^{-1}. Mass spectrum (positive-ion FAB): m/z 458 $[L^6+H]^+$, m/z 441 $[L^6-CH_3]^+$. Electron Impact: m/z 441 (L^6-CH_3); UV–Vis spectrum (in CH_3CN), (λ (nm), ε (M^{-1} cm^{-1})): (251, 16 066); (303, 5930).

The ligand is air stable, soluble in acetonitrile, absolute ethanol, chloroform, dimethylformamide, dimethyl sulfoxide, pyridine; moderately soluble in dichloromethane, and insoluble in benzene, toluene, diethyl ether, petroleum ether and water.

2.3. Synthesis of copper(II) complexes

2.3.1. General procedure for complexes with Schiff-base macrocycles L^1–L^6

A solution of the hydrated copper nitrate or perchlorate (1 mmol) in hot methanol, absolute ethanol or acetonitrile was added to a refluxing solution of corresponding dialdehyde (1 mmol) (25 cm^3) in the same solvent (15 cm^3). The solution was magnetically stirred and heated, and a methanolic or ethanolic solution of corresponding diamine (1 mmol) was slowly added. Refluxing continued for ca. 2.5–5 h. The solution was then concentrated in a rotary evaporator to ca. 10–15 cm^3. A small volume of diethyl ether (ca. 2–5 cm^3) was slowly infused into the solution producing powdery precipitates. The products were filtered off, washed with cold ethanol or methanol, then diethyl ether and dried in vacuo. The compounds are air stable, soluble in acetonitrile, methanol, dimethylformamide, dimethyl sulfoxide, pyridine, dichloromethane, nitrobenzene and nitromethane and insoluble in diethyl ether, water, chloroform and cyclohexane.

For the synthesis of L^4, the order of the reagent addition was modified. A solution of the hydrated copper nitrate or perchlorate (1 mmol) in methanol (15 cm^3) was added to a refluxing solution of tris(2-aminoethyl)amine (1 mmol) in the same solvent (25 cm^3). The solution was magnetically stirred and heated while a methanolic solution of dialdehyde (1 mmol) was slowly added. Refluxing was continued for ca. 4 h. Within 2 h a blue precipitate began to deposit. After cooling to room temperature, the product was filtered off and dried in vacuo. The microanalytical data for this product were close to that of the corresponding complex between the metal and free amine.

The filtrate was then concentrated in a rotary evaporator to ca. 10–15 cm^3. An equal volume of diethyl ether was slowly infused into the solution producing powdery precipitates. A second pale green product was filtered off, washed with cold absolute ethanol and dried in vacuo. Both compounds are air stable, soluble in acetonitrile, methanol, dimethylformamide, dimethyl sulfoxide, pyridine, dichloromethane, nitrobenzene and nitromethane, and insoluble in diethyl ether, water, chloroform and cyclohexane.

2.3.1.1. [L^{1}Cu](NO$_3$)$_2$·3H$_2$O. Yield 40%. Microanalysis (%) (Found: C, 52.75; H, 4.80; N, 8.85. $C_{37}H_{39}N_5O_{14}Cu$ requires C, 52.80; H, 4.65; N, 8.30%); m.p. 250–300 °C (dec.); IR (KBr disc): ν(C=N)$_{\mathrm{imi}}$ 1642 cm^{-1} ν(C=N)$_{\mathrm{py}}$ 1596–1459 cm^{-1}, ν(NO$_3$) 1384, 1240, 849, 764, 751 cm^{-1}; FAB MS (*m/z*, *M*$^+$): 600 [L^1+H]$^+$; 663 [CuL^1]$^+$. UV–Vis in CH$_3$CN (λ, nm): bands at 252(sh) ($\varepsilon \approx 22\,421$ M^{-1} cm^{-1}); 314, ($\varepsilon \approx 16\,325$ M^{-1} cm^{-1}); 383(sh), ($\varepsilon \approx 12\,171$ M^{-1} cm^{-1}). Λ_M (DMF): 89 Ω^{-1} cm^2 mol^{-1}. Colour: dark green. µD (BM): 1.67.

2.3.1.2. [L^{1}Cu$_2$](ClO$_4$)$_4$ 5H$_2$O. Yield 35%. Microanalysis (%) (Found: C, 36.70; H, 4.00; N, 3.75. $C_{37}H_{43}N_3O_{26}Cl_4Cu_2$ requires C, 36.60; H, 3.55; N, 3.45%); IR (KBr disc): ν(C = N)$_{\mathrm{imi}}$ 1640 cm$^{-1,}$ ν(C=N)$_{\mathrm{py}}$ 1601, 1450 cm^{-1}, ν(ClO$_4$) 1121, 1087, 639, 624 cm^{-1}; FAB MS (*m/z*, *M*$^+$): 600 [L^1+H]$^+$; 663 [CuL^1]$^+$, 827 [Cu$_2$L^1(ClO$_4$)]$^+$. UV–Vis in CH$_3$CN (λ, nm): bands at 253 ($\varepsilon \approx 16\,797$ M^{-1} cm^{-1}); 314, ($\varepsilon \approx 11\,364$ M^{-1} cm^{-1}); 396, ($\varepsilon \approx 8222$ M^{-1} cm^{-1}). Λ_M (DMF): 106 Ω^{-1} cm^2 mol^{-1}. Colour: brown. µD (BM): 1.5.

2.3.1.3. [L^{2}Cu](NO$_3$)$_2$·2H$_2$O. Yield 27%. Microanalysis (%) (Found: C, 54.15; H, 5.10; N, 8.90. $C_{37}H_{37}N_5O_{13}Cu$ requires C, 54.00; H, 4.55; N, 8.50%); m.p. ~ 300 °C (dec.); IR (KBr disc): ν(C=N)$_{\mathrm{imi}}$ 1639 cm$^{-1,}$ ν(C=N)$_{\mathrm{py}}$ 1602–451 cm^{-1}, ν(NO$_3$) 1384, 1303, 1047, 839, 757 cm^{-1}; FAB MS (*m/z*, *M*$^+$): 600 [L^2+H]$^+$; 663 [CuL^2]$^+$. Λ_M (CH$_3$CN): 165 Ω^{-1} cm^2 mol^{-1}. Colour: green.

2.3.1.4. [L^{2}Cu](ClO$_4$)$_2$·H$_2$O. Yield 39%. Microanalysis (%) (Found: C, 50.40; H, 4.45; N, 4.40. $C_{37}H_{35}N_3O_{14}Cl_2Cu$ requires C, 50.50; H, 4.00; N, 4.70%); IR (KBr disc): ν(C=N)$_{\mathrm{imi}}$ 1662 cm^{-1}, ν(C=N)$_{\mathrm{py}}$ 1600–1452 cm^{-1}, ν(ClO$_4$) 1121, 1087, 1047, 636, 624 cm^{-1}; FAB MS (*m/z*, *M*$^+$): 600 [L^2+H]$^+$; 663 [CuL^2]$^+$. Λ_M (CH$_3$CN): 147 Ω^{-1} cm^2 mol^{-1}. Colour: dark green.

2.3.1.5. [L^{3}Cu$_2$](ClO$_4$)$_4$·3H$_2$O. Yield 30%. Microanalysis (%) (Found: C, 39.85; H, 3.85; N, 5.20. $C_{40}H_{38}N_4O_{23}Cl_4Cu_2$ requires C, 39.65; H, 3.16; N, 4.65%); IR (KBr disc): ν(C=N)$_{\mathrm{imi}}$ 1643 cm$^{-1,}$ ν(C=N)$_{\mathrm{py}}$ 1601, 1454 cm^{-1}, ν(ClO$_4$) 1121, 1097, 639, 624 cm^{-1}; FAB MS (*m/z*, *M*$^+$): 633 [L^3+H]$^+$; 696 [CuL^3]$^+$. Reflectance diffuse (nm): 318, 408, 621. Λ_M (CH$_3$CN): 239 Ω^{-1} cm^2 mol^{-1}. Colour: green.

2.3.1.6. [L^{4}Cu](ClO$_4$)$_2$·7H$_2$O. Yield 22%. Microanalysis (%) (Found: C, 38.80; H, 4.95; N, 8.30. $C_{27}H_{45}N_5O_{17}Cl_2Cu$ requires C, 38.35; H, 5.35; N, 8.25%); IR (KBr disc): ν(C=N)$_{\mathrm{imi}}$ 1642 cm$^{-1,}$ ν(C=N)$_{\mathrm{py}}$ 1593, 1445 cm^{-1}, ν(ClO$_4$) 1146, 1088, 637, 627 cm^{-1}; FAB MS (*m/z*, *M*$^+$): 539 [CuL^4(H$_2$O)]$^+$; 639 [CuL^4(ClO$_4$)(H$_2$O)]$^+$. UV–Vis in CH$_3$CN (λ, nm): bands at 269 ($\varepsilon \approx 10\,944$ M^{-1} cm^{-1}); 315(sh), ($\varepsilon \approx 4873$ M^{-1} cm^{-1}); 633(w), ($\varepsilon \approx 157$ M^{-1} cm^{-1}). Λ_M (CH$_3$CN): 159 Ω^{-1} cm^2 mol^{-1}. Colour: blue greenish.

2.3.1.7. [L^{5}Cu$_2$](NO$_3$)$_4$·0.5H$_2$O. Yield 59%. Microanalysis (%) (Found: C, 43.45; H, 4.00; N, 8.20. $C_{34}H_{35}N_6O_{18.5}Cu_2$ requires C, 43.00; H, 3.70; N, 8.85%); m.p. 185–200 °C (dec.); IR (KBr disc): ν(C=N)$_{\mathrm{imi}}$ 1641 cm$^{-1,}$ ν(C=C)$_{\mathrm{phenyl}}$ 1603, 1452 cm^{-1}, ν(NO$_3$) 1384, 1303, 1245, 838, 814, 754 cm^{-1}; FAB MS (*m/z*, *M*$^+$): 567 [L^5+H]$^+$; 880 [Cu$_2$L^5(NO$_3$)$_3$]$^+$, UV–Vis in CH$_3$CN (λ, nm): bands at 275(sh) ($\varepsilon \approx 11\,488$ M^{-1} cm^{-1}); 321, ($\varepsilon \approx 9535$ M^{-1} cm^{-1}); 372(sh), ($\varepsilon \approx 8538$ M^{-1} cm^{-1}); 594(sh), ($\varepsilon \approx 1632$

M^{-1} cm^{-1}). Λ_M (CH_3CN): 238 Ω^{-1} cm^2 mol^{-1}. Colour: dark green. μD (BM): 2.64 (1.87/Cu^{2+}).

2.3.1.8. $[L^5Cu](ClO_4)_2\cdot0.5CH_3CN$. Yield 36%. Microanalysis (%) (Found: C, 49.60; H, 4.00; N, 3.65. $C_{35}H_{35.5}N_{2.5}O_{14}Cl_2Cu$ requires C, 49.50; H, 4.20; N, 4.10%); IR (KBr disc): ν(C=N)$_{imi}$ 1641 cm^{-1}, ν(C=N)$_{phenyl}$ 1598, 1453 cm^{-1}, ν(ClO_4) 1120, 1085, 636, 624 cm^{-1}; FAB MS (*m*/*z*, *M*$^+$): 567 [L^5+H]$^+$; 630 [CuL^5]$^+$. UV–Vis in CH_3CN (λ, nm): bands at 277(sh) ($\varepsilon \approx 14719$ M^{-1} cm^{-1}); 317, ($\varepsilon \approx 14871$ M^{-1} cm^{-1}); 393(sh), ($\varepsilon \approx 10791$ M^{-1} cm^{-1}); 591(sh), ($\varepsilon \approx 2419$ M^{-1} cm^{-1}). Λ_M (CH_3CN): 173 Ω^{-1} cm^2 mol^{-1}. Colour: dark brown.

2.3.1.9. $[L^6Cu](ClO_4)_2\cdot5H_2O$. Yield 81%. Microanalysis (%) (Found: C, 41.85; H, 5.85; N, 6.80. $C_{28}H_{42}N_4O_{15}Cl_2Cu$ requires C, 41.60; H, 5.20; N, 6.90%); IR (KBr disc): ν(C=N)$_{imi}$ 1620 cm$^{-1,}$ ν(C=N)$_{Py}$ 1597, 1456 cm^{-1}, ν(ClO_4) 1121, 1092, 636, 628 cm^{-1}; FAB MS (*m*/*z*, *M*$^+$): 457 [L^6+H]$^+$; 521 [CuL^6]$^+$. Λ_M (CH_3CN): 142 Ω^{-1} cm^2 mol^{-1}. Colour: blue.

2.3.2. General procedure for complexes with diaminic macrocycles L^7 and L^8

The appropriate metal nitrate or perchlorate (0.10 mmol) was dissolved in methanol (50 cm^3) and slowly added to a stirred and refluxing solution (25 cm^3) of the appropriate ligand (0.10 mmol) in methanol (L^7) or 1:1 chloroform/benzene (L^8). An immediate colour change was usually apparent. The mixture was stirred during 72 h at room temperature. Products either precipitated directly after filtration or after the volume of the filtrate cold solution had been reduced. The products were filtered off, washed with cold absolute ethanol, then diethyl ether and dried in vacuum. The complexes are air stable, soluble in dimethylformamide, dimethyl sulfoxide and acetonitrile, and insoluble in absolute ethanol, diethyl ether and water.

2.3.2.1. $[L^7Cu_2](NO_3)_4\cdot5H_2O$. Yield 35%. Microanalysis (%) (Found: C, 42.35; H, 4.55; N, 9.50. $C_{37}H_{47}N_7O_{22}Cu_2$ requires C, 41.60; H, 4.45; N, 9.20%); IR (KBr disc): ν(C=N)$_{py}$ 1602, 1451 cm^{-1}, ν(NO_3) 1384, 1287, 826, 752 cm^{-1}; FAB MS (*m*/*z*, *M*$^+$): 604 [L^7+H]$^+$; 666 [CuL^7]$^+$; 749 [$Cu_2L^7(H_2O)$]$^+$; 916 [$Cu_2L^7(NO_3)_3H$]$^+$; Λ_M (MeCN): 247 Ω^{-1} cm^2 mol^{-1}. Colour: brown.

2.3.2.2. $[L^7Cu](ClO_4)_2\cdot6Et_2O$. Yield 69%. Microanalysis (%) (Found: C, 56.10; H, 7.65; N, 3.80. $C_{61}H_{97}N_3O_{19}Cl_2Cu$ requires C, 55.90; H, 7.45; N, 3.20%); IR (KBr disc): ν(C=N)$_{py}$ 1600, 1451 cm^{-1}, ν(ClO_4) 1118, 1047, 636, 626 cm^{-1}; FAB MS (*m*/*z*, *M*$^+$): 604 [L^7+H]$^+$, 667 [CuL^7]$^+$. UV–Vis in CH_3CN (λ, nm): bands at 248 ($\varepsilon \approx 39475$ M^{-1} cm^{-1}); 294, ($\varepsilon \approx 13417$ M^{-1} cm^{-1}); 321 ($\varepsilon \approx 7438$ M^{-1} cm^{-1}). Λ_M (MeCN): 218 Ω^{-1} cm^2 mol^{-1}. Colour: olive-green.

2.3.2.3. $[L^8Cu_2](NO_3)_4\cdot2H_2O$. Yield 21%. Microanalysis (%) (Found: C, 41.60; H, 4.20; N, 8.25. $C_{34}H_{42}N_6O_{20}Cu_2$ requires C, 41.60; H, 4.30; N, 8.55%); IR (KBr disc): ν(C=N)$_{phenyl}$ 1600, 1451 cm^{-1}, ν(NO_3) 1384, 1287, 836, 752 cm^{-1}; FAB MS (*m*/*z*, *M*$^+$): 571 [L^8+H]$^+$. UV–Vis in CH_3CN (λ, nm): bands at 254 ($\varepsilon \approx 6034$ M^{-1} cm^{-1}); 314, ($\varepsilon \approx 3795$ M^{-1} cm^{-1}); 382 ($\varepsilon \approx 2222$ M^{-1} cm^{-1}). Λ_M (CH_3CN): 162 Ω^{-1} cm^2 mol^{-1}. Colour: dark green. μD (BM): 3.02.

2.3.2.4. $[L^8Cu](ClO_4)_2\cdot2CHCl_3$. Yield 61%. Microanalysis (%) (Found: C, 36.60; H, 4.10; N, 2.85. $C_{34}H_{40}N_2O_{14}Cl_8Cu_2$ requires C, 36.75; H, 3.60; N, 2.50%); IR (KBr disc): ν(C=N)$_{phenyl}$ 1599, 1456 cm^{-1}, ν(ClO_4) 1121, 1108, 1090, 636, 628 cm^{-1}; FAB MS (*m*/*z*, *M*$^+$): 571 [L^8+H]$^+$. Λ_M (CH_3CN): 125 Ω^{-1} cm^2 mol^{-1}. Colour: blue greenish.

2.3.3. Transmetallation reaction of $[L^1La](ClO_4)_3\cdot4H_2O$ with $Cu(ClO_4)_2\cdot6H_2O$

The complex $[L^1La](ClO_4)_3\cdot4H_2O$ was prepared as previously described in Ref. [29]. A solution of Cu(II) perchlorate (0.15 mmol) in absolute ethanol (30 cm^3) was added dropwise to a solution of $[L^1La](ClO_4)_3\cdot4H_2O$ (0.15 mmol) in methanol (30 cm^3). The reaction was then heated (~ 50 °C) for 2 h, after which time the product $[L^1Cu_2](ClO_4)_4\cdot2H_2O$ was collected by filtration as a brown greenish powder. The solid was washed with cold methanol and diethyl ether. Yield 0.042 g, 48%. Microanalysis (%) (Found C, 38.80; H, 3.60; N, 3.65. $C_{37}H_{37}N_3O_{23}Cl_4Cu_2$ requires C, 38.30; H, 3.20; N, 3.60%); IR (KBr disc): ν(C=N)$_{imi}$ 1639 cm^{-1}, ν(C=N)$_{Py,}$ ν(C=C)$_{phenyl}$ 1603 and 1452 cm^{-1}, ν(ClO_4) 1121, 1109, 1088 and 624 cm^{-1}; FAB MS (*m*/*z*, *M*$^+$): 600 [L^1+H]$^+$; 726 [Cu_2+L^1]$^+$. The molar conductivity of the complex, 205.8 Ω^{-1} cm^2 mol^{-1} in acetonitrile at 25 °C, is in the range reported for 1:2 electrolytes in this solvent [32] Fig. 2.

3. Results and discussion

3.1. Synthesis and characterisation of the diiminic macrocycles L^4 and L^6

Our research group has already reported the synthesis of Schiff-base macrocycles derived from the direct cyclocondensation of α,ω-diamines with the dialdehyde 2,6-bis(2-formylphenoxymethyl)pyridine [29,33]. Similar reactions between tris(2-aminoethyl)amine or *N*,*N*-bis(3-aminopropyl)methylamine and 2,6-bis(2-formylphenoxymethyl)pyridine resulted on the isolation of

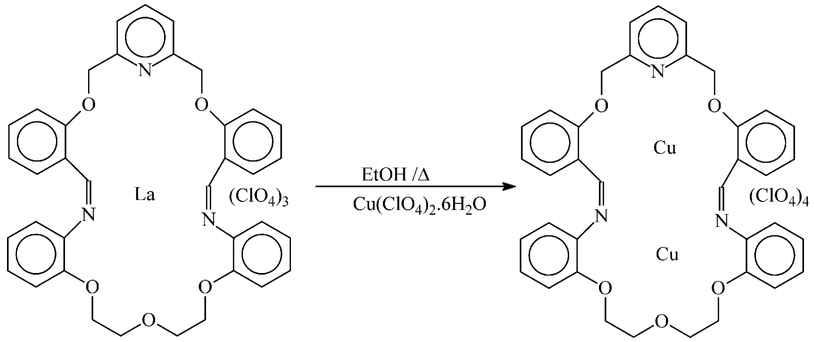

Fig. 2. Scheme of the transmetallation reaction of $[LaL^1](ClO_4)_3 \cdot 4H_2O$ with $Cu(ClO_4)_2 \cdot 6H_2O$ in absolute ethanol/methanol.

yellow powdery solids characterised as the macrocycles L^4 and L^6. The IR spectra show intense absorption bands at 1662 (L^4) and 1636 (L^6) cm $^{-1}$, corresponding to an imine bond, and no peaks assignable to unreacted amine or carbonyl groups. The highest peaks in the FAB mass spectra are at 457 (L^4) and 457 (L^6) amu, corresponding to $1+1$ cyclocondensation products. Satisfactory elemental analysis data have been also obtained. Recently, Fenton and Nájera also reported the synthesis of L^4 macrocycle using $Ba(SCN)_2$ as template agent [34]. The Schiff-base ligand L^6 was studied by NMR Cosy45, Dept135 and HMQC in $CDCl_3$. The ^1H NMR spectrum in $CDCl_3$ shows a peak at 8.80 ppm, corresponding to the imine protons (Table 1, Fig. 3). Unfortunately, the poor solubility of L^4 made impossible its study by NMR spectroscopy.

3.2. Copper(II) complexes

Template reaction between equimolar amounts of 2,6-bis(2-formylphenoxymethyl)pyridine (L^1, L^3, L^4, and L^6) or 1,7-bis(2′-formylphenyl)-1,4,7-trioxaheptane (L^2 and L^5), the corresponding diamine precursor, and copper(II) nitrate or perchlorate, under the conditions described in Section 2, gave analytically pure products formulated as mononuclear complexes, $[L^mCu](NO_3)_2 \cdot xH_2O \cdot (L^m = L^1$ and $L^2)$; $[L^mCu](ClO_4)_2 \cdot xH_2O \cdot yCH_3CN$ ($L^m = L^2$, L^4, L^5 and L^6) and dinuclear complexes $[L^5Cu_2](NO_3)_4 \cdot 0.5H_2O$; $[L^mCu_2](ClO_4)_4 \cdot xH_2O$ ($L^m = L^1$ and L^3). Direct reaction between the free macrocycles L^7 and L^8 and copper(II) salts gave analytically pure products with formula $[L^mCu_2](NO_3)_4 \cdot xH_2O$ ($L^m = L^7$ and L^8) and $[L^mCu](ClO_4)_2 \cdot y$solvent ($L^m = L^7$ and L^8). The analytical and conductivity data for the complexes are presented in Section 2. For the dinuclear complexes, both elemental analysis and FAB spectral data were in accordance with the general formula $[LCu_2](X)_n \cdot xH_2O$; attempts to obtain the corresponding mononuclear complexes were unsuccessful. For the ligands L^3, L^4 and L^6, the complexation reactions with the hydrated copper(II) nitrate were unsuccessful, and only a mixture of reagents and products were recovered.

Table 2
Crystal data and structure refinement for $C_{13}H_{28}ClCu_2N_3O_{10}$

Empirical formula	$C_{13}H_{28}ClCu_2N_3O_{10}$
Formula weight	548.91
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Space group	$P2_1/n$
Crystal system	monoclinic
Unit cell dimensions	
a (Å)	9.6703
b (Å)	12.4001
c (Å)	18.1910
α (°)	90
β (°)	99.0070
γ (°)	90
V (Å^3)	2154.4(2)
Z	4
D_{calc} (Mg m^{-3})	1.692
Absorption coefficient (mm^{-1})	2.152
$F(0\,0\,0)$	1128
Crystal size (mm)	$0.12 \times 0.10 \times 0.05$
θ Range for data collection (°)	2.00–28.30
Index ranges	$12 \le h \le 6$, $-15 \le k \le 16$, $-24 \le l \le 24$
Reflections collected	11565/5274 [$R_{int} = 0.0976$]
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	5274/0/262
Goodness-of-fit on F^2	0.998
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0718$, $wR_2 = 0.1380$
R indices (all data)	$R_1 = 0.1726$, $wR_2 = 0.1772$
Largest difference peak and hole (e Å^{-3})	0.680 and $y - 0.558$

In an attempt to synthesise the corresponding mononuclear Cu(II) perchlorate complex with L^1 macrocycle, we tried to obtain it by transmetallation reaction of the complex $[L^1La](ClO_4)_3 \cdot 4H_2O$ in the presence of $Cu(ClO_4)_2$. Again, the dinuclear copper(II) complex was isolated; data for this complex are given in Section 2. The La(III) complex undergoes a transmetallation reaction, and the La(III) ion can be easily replaced by two Cu(II) ions; this suggests the lability of the La(III) complex, as well as capability of L^1 to accommodate two Cu(II) atoms.

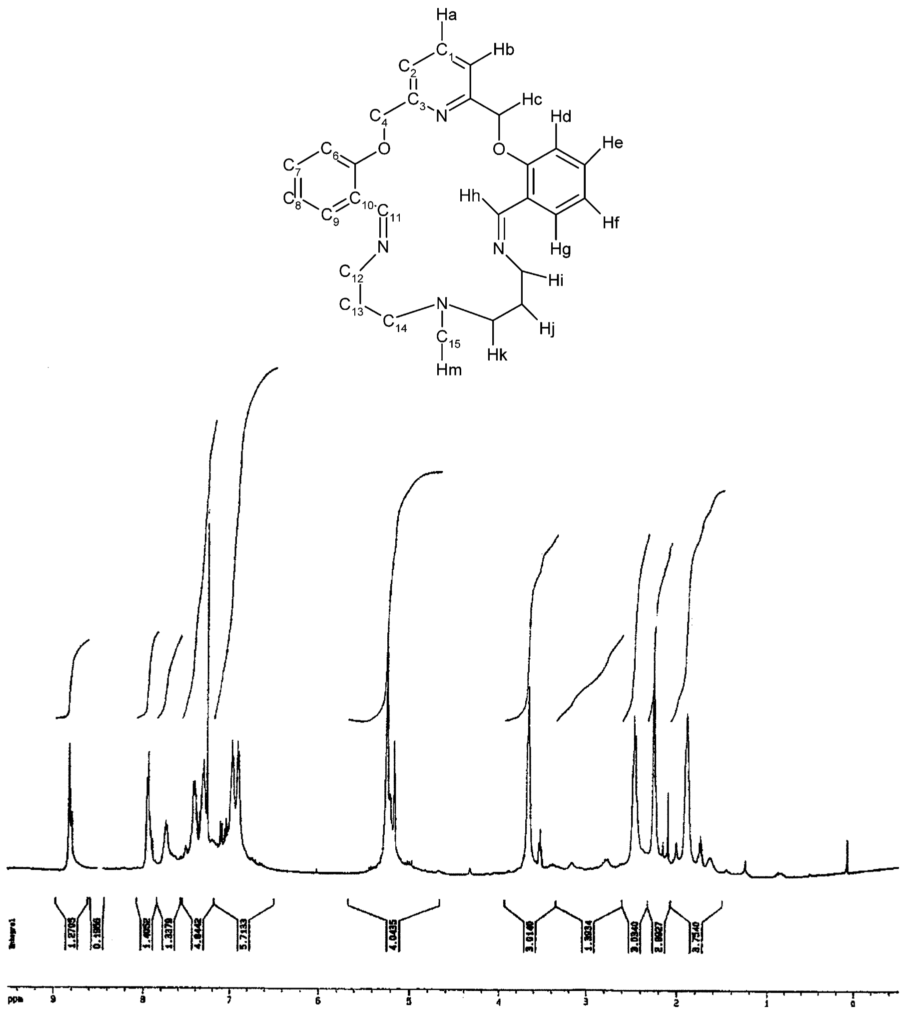

Fig. 3. ^{1}H NMR spectrum of L^6 in $CDCl_3$ at room temperature, recorded in a BRUKER AMX 500 MHz.

For the complexes with L^2–L^8, the molar conductivity data were determined in CH_3CN; for L^1, the solvent utilised was DMF. The values obtained for all the mononuclear complexes are in the range reported for 1:1 electrolytes in these solvents; for the binuclear complexes the data are in the range reported for 1:2 electrolytes [32]. These results suggest that one or two counterions are coordinated, at least in these solvents, and also most likely in the solid state.

The FAB mass spectra feature in all cases peaks at m/z 600 ($[L^1+H]^+$), m/z 600 ($[L^2+H]^+$) m/z 633 ($[L^3+H]^+$), m/z 457 ($[L^4+H]^+$), m/z 567 ($[L^5+H]^+$), m/z 457 ($[L^6+H]^+$), m/z 604 ($[L^7+H]^+$) and m/z 571 ($[L^8+H]^+$) as the most intense ones, confirming the stability of the macrocycles in the metal complexes. Peaks attributable to the fragments $[CuL^m]^+$ can be observed for the complexes with L^1, L^2, L^3, L^4, L^5, L^6 and L^7. The spectra for the dinuclear complexes feature peaks attributable to the species $[Cu_2L^1(ClO_4)]^+$, $[Cu_2L^5(NO_3)_3]^+$, $[Cu_2L^7(H_2O)]^+$ and $[Cu_2L^7(NO_3)_3]^+$.

The IR spectra confirm the existence of the cyclic ligands in the complexes, with the presence of absorption bands due to imine groups at ca. 1662–1640 cm^{-1}, and the absence of bands due to ν(C=O) or ν(NH_2) [35]. All spectra exhibit medium to strong bands at ca. 1600 and 1455 cm^{-1} as expected for the two highest-energy pyridine or benzene ring vibrations [36]. A broad absorption band in the region 3450–3385 cm^{-1} present in the majority of the complexes is probably due to the existence of lattice and/or coordinated water in the molecules [37]. In the case of the diamine complexes with L^7 and L^8 bands attributable to ν(NH) cannot be observed due the existence of the broad band at ca. 3450 as mentioned above.

The absorptions of the counterions (NO_3^- or ClO_4^-) provide some useful structural information. The IR spectra for all nitrate complexes show bands at ca. 1460–1452 (ν_5), 1300(ν_1) and 1028(ν_2) cm^{-1}, suggesting the presence of coordinated nitrate groups, as well as a band at ca. 1384 cm^{-1} attributable to ionic NO_3^- [38,39]. In absence of crystal structures, it is difficult to distinguish between mono- and bi-dentate chelating nitrates; however, the separation ν_5–ν_1 can be used as a near criterion to distinguish between the degree of covalence of the nitrate coordination [40]. The magnitude of this value (ca. 160 cm^{-1}) is indicative of a bidentate interaction [41].

The IR spectra of the perchlorate complexes were assigned by comparison with similar macrocyclic complexes previously reported [42–45]. All spectra exhibit bands attributable to the asymmetric Cl–O stretching mode (ν_3) at ~1088 cm^{-1} and the asymmetric Cl–O bending mode (ν_4) at ~627 cm^{-1}. The higher-energy band shows considerable splitting, with three maxima at ~1050, 1088 and 1121 cm^{-1}, suggesting some interaction of at least one of the ClO_4^- anions with the metal. The high intensity of the peak at 1087 cm^{-1} compared to those of the side peaks at 1120 and 1040 cm^{-1} may be indicative the coexistence of ionic perchlorate in the complexes. However, it must be pointed out that the C–O–C stretching mode of the polyether chains of the complexes with L^1, L^2, L^5, L^7 and L^8 also falls in this region.

The electronic spectra for some complexes with L^1, L^4, L^5, L^7 and L^8 were measured at room temperature, using acetonitrile solutions; the data obtained for each one are summarized in Section 2. In general, the spectra present bands at ca. 252, 315 and 392 nm. In all cases, these bands are associated with the π–π* and n–π* electronic transitions of the chromophores present in the macrocyclic skeletons [46]. The spectra for some of these complexes were also recorded in DMF and $CHCl_3$, in an attempt to confirm the π–π* or n–π* nature of these bands, by observing their position in different solvents; unfortunately, the co-presence of different kind of chromophores, such as imine groups, phenyl and/or pyridine rings, made impossible to differentiate the exact nature of the bands.

In some cases, the intensity of the absorption bands changed when the spectra were recorded after a period of 1 week, suggesting the displacement of some coordinated anions or water molecules by solvent molecules, or a demetallation process. The strong absorption bands present in the complexes required the use of concentrations in the range 10^{-6} to 10^{-4} M; unfortunately, in this range it was not possible to observe the d–d bands attributable to metal transitions for the majority of the complexes. Only the spectra of the complexes $[L^4Cu](ClO_4)_2\cdot 7H_2O$, $[L^5Cu_2](NO_3)_4\cdot 0.5H_2O$ and $[L^5Cu](ClO_4)_2\cdot 0.5CH_3CN$ exhibit a band at 633, 594 and 591 nm, respectively, assignable to the d–d transitions band of the copper(II) ions.

The diffuse reflectance spectrum for the complex $[L^3Cu_2](ClO_4)_4\cdot 3H_2O$ features two bands at ca. 318 and 408 nm, and a broad band a 621 nm. The first two bands, in the ultraviolet region, can be assigned to the π–π* and n–π* electronic transitions in the chromophores present in the macrocyclic ligand. The position of the broad band observed in the visible region suggests a six coordination number for each metal centre; however, due the Jahn–Teller effect present in the Cu(II) complexes, this band could also be indicative of distorted tetragonal symmetry for each copper centre [47].

Magnetic susceptibility measurements were recorded at room temperature for the complexes $[L^1Cu](NO_3)_2\cdot 3H_2O$, $[L^1Cu_2](ClO_4)_4\cdot 5H_2O$, $[L^5Cu_2](NO_3)_4\cdot 0.5H_2O$ and $[L^8Cu_2](NO_3)_4\cdot 2H_2O$. The values of μD calculated for these complexes are 1.67, 1.5, 2.64 and 3.02 BM, respectively, suggesting a six coordination index for Cu(II) in all the complexes; these values are fairly close to those observed for other copper(II) macrocyclic complexes [48]. The low μD values suggest some antiferromagnetic interactions in these binuclear complexes [49].

In absence of crystal structures, we must be careful in any attempt to elucidate the coordinative environment of the Cu(II) ions on these systems. Taking into account that there are eight donor atoms in the macrocyclic ligands, and that the spectroscopic data suggest the presence of at least one or two coordinated counterions, it could be suggested a distorted octahedral or tetragonal environment for each metal, which would be in agreement with the UV–Vis data and magnetic moments calculated.

The electrochemical properties of the complexes $[L^1Cu_2](ClO_4)_4\cdot 5H_2O$, $[L^1Cu](NO_3)_2\cdot 3H_2O$, $[L^4Cu](ClO_4)_2\cdot 7H_2O$, $[L^5Cu_2](NO_3)_4\cdot 0.5H_2O$, and $[L^8Cu_2](NO_3)_4\cdot 2H_2O$ were studied by cyclic voltammetry in dry acetonitrile solutions, of concentration 10^{-3} mol dm^{-3}, containing NEt_4ClO_4 at 0.1 mol dm^{-3} as supporting electrolyte, and at scan rate of 20 mV s^{-1}. The cyclic voltammograms for all the complexes are very similar, involving two clearly distinguishable redox processes at a positive (between +0.8 and +0.7 V, irreversible) and a negative (between −0.3 and −0.2 V irreversible) potentials. These processes are assigned to two successive one-electron oxidation/reduction steps, i.e. Cu(I)–Cu(II) and Cu(II)–Cu(I), respectively, with respect to a saturated calomel electrode [50]. The negative peak for the binuclear complex $[L^5Cu_2](NO_3)_4\cdot 0.5H_2O$ is split in two, at −0.3 and −0.1 V, suggesting the existence of processes Cu(II)–Cu(I) and Cu(I)–Cu(0). The irreversibility observed in the CV suggests the presence of reactions leading to the cleavage of the macrocyclic devices; a similar result has been reported for a related macrocyclic lanthanide complexes [29].

3.3. Crystal structure of $[CuL^9(CH_3COO)Cu(CH_3COO)_2]ClO_4$, $L^9 = NH_2(CH_2)_3NHCH_3(CH_2)_3NH_2$

By evaporation of an acetonitrile solution of $[L^6Cu](ClO_4)_2\cdot 5H_2O$, with slow diffusion of chloroform/diethyl ether, and in the presence of acetic acid solution 15%, two types of crystals, pale blue and

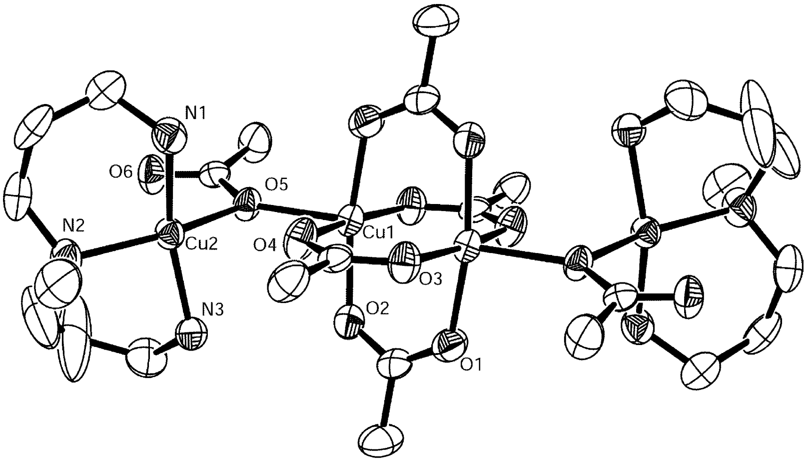

Fig. 4. Crystal structure and selected bond lengths (Å) and angles (°) for the coordination tetramer. Cu(1)–O(1)#1 1.944(5), Cu(1)–O(2) 1.961(5), Cu(1)–O(3)#1 1.964(5), Cu(1)–O(4) 2.001(5), Cu(1)–O(5) 2.140(4), Cu(2)–N(3) 1.990(6), Cu(2)–N(1) 1.992(6), Cu(2)–O(5) 2.018(4), Cu(2)–N(2) 2.038(6), O(1)#1–Cu(1)–O(2) 168.8(2), O(1)#1–Cu(1)–O(3)#1 88.1(2), O(2)–Cu(1)–O(3)#1 92.3(2), O(1)#1–Cu(1)–O(4) 90.9(2), O(2)–Cu(1)–O(4) 86.8(2), O(3)#1–Cu(1)–O(4) 169.28(19), O(1)#1–Cu(1)–O(5) 95.67(19), O(2)–Cu(1)–O(5) 94.94(18), O(3)#1–Cu(1)–O(5) 106.48(17), O(4)–Cu(1)–O(5) 84.24(18), N(3)–Cu(2)–N(1) 163.1(2), N(3)–Cu(2)–O(5) 88.5(2), N(1)–Cu(2)–O(5) 90.9(2), N(3)–Cu(2)–N(2) 91.8(2), N(1)–Cu(2)–N(2) 95.3(2), O(5)–Cu(2)–N(2) 156.8(2). Symmetry transformations used to generate equivalent atoms: #1 $-x+2$, $-y+2$, $-z$.

intense dark blue ones, were obtained. The IR spectrum of the pale blue crystals features bands attributable to the presence of iminic and aromatic groups in the macrocycle. Unfortunately, these crystals proved unsuitable for X-ray analysis.

The IR spectrum of the dark blue crystals do not show any band attributable the iminic bond, indicating a possible rupture of the ligand in the presence of acidic media. These crystals were found to be suitable for X-ray analysis. The crystal structure shows a new copper(II) complex formed with the free diamine *N*,*N*-bis(3-aminopropyl)methylamine and acetate groups, confirming the instability of the Schiff-base macrocycle in the acidic conditions. Fig. 4 shows the structure for this new copper(II) complex.

The coordination environment for the Cu(2) is formed by three nitrogen atoms from the diamine and an oxygen atom from one acetate group, which bridges with the Cu(1), showing a four coordination index in a very distorted square geometry. The second metal centre, Cu(1), has a five coordinative index formed by five oxygen atoms from five acetate groups, four of them acting as bidentate bridging between two Cu(1) metal centres and the fifth bridging between Cu(1) and Cu(2) through O(5). The coordination polyhedron may be described as a distorted square pyramid.

The tetramer unit is formed by two binuclear subunits, with a metal–metal distance between Cu(1) and Cu(1_3) of 2.5944 Å. This value is typical for the distance observed in structures with Cu–Cu interactions [51–54].

McCasland and Alcok had found similar results with other macrocycles derived from the same diamine precursor [55].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 205991. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-366033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.uk).

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