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A tris-imidazolecarboxyaldehyde copper(II) complex with unusual carbonyl co-ordination: structure and reactivity

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4-Methyl-5-imidazolecarboxyaldehyde (HL^1) reacts with copper(II) perchlorate to give the complex $[Cu(HL^1)_3](ClO_4)_2$. Its X-ray structure reveals that three ligands are bonded to the copper(II) ion in a bidentate chelate fashion through the imidazole nitrogens and aldehyde oxygen atoms, leading to a CuN_3O_3 chromophore. Carbonyl co-ordination to copper(II) is not usual, in fact there are very few reported examples of structurally characterised complexes of this type. When $[Cu(HL^1)_3](ClO_4)_2$ is dissolved in a KOH-containing methanol solution, the polymer $[Cu(L^1)_2]_n$ precipitates. The magnetic properties of $[Cu(L^1)_2]_n$ are typical of an imidazolate-bridged copper(II) system in which the bridge involves equatorial positions on the copper(II) co-ordination polyhedra. A J value of -58.1 cm^{-1} was calculated by application to the experimental data of the theoretical equation for a uniform one-dimensional infinite chain system. Additionally, the co-ordinated carbonyl groups of $[Cu(HL^1)_3](ClO_4)_2$ react with 1,3-diaminopropane, leading to a new monomeric Schiff-base copper(II) complex. However, this reaction does not take place when the diamine is 1,2-diaminopropane, which is likely due to the sterically promoted low reactivity for imine bond formation with the $-NH_2$ group close to the methyl substituent in 1,2-diaminopropane.

Introduction

Imidazole and imidazolyl-containing ligands have been widely used in co-ordination chemistry due to their versatility in the production of polymetallic complexes, which are of interest both in magnetochemistry, as a consequence of the significant magnetic interaction mediated when the imidazolate group bridges two paramagnetic metal ions,[1] and in connection with the design of model compounds mimicking the structure of bimetallic active sites present in some metalloproteins, the family of superoxidodismutases being a good example.[2] Moreover, the interaction of copper ions with the imidazole group of histidine residues has been observed in many biological molecules which gives additional interest to the preparation of mononuclear imidazole copper(II) complexes.[3]

One of the most often used strategies for the incorporation of an imidazolyl moiety into a ligand is the condensation of an appropriate mono- or diamine with an imidazolecarboxyaldehyde. The Schiff-base ligands thus obtained contain designed co-ordination sites formed by the imidazole and imine nitrogen atoms. The copper(II) complexes of this kind of ligand are able to undergo reversible interconversion between monomer and self-assembled oligomer by inputting external information, specifically a change of pH.[4] By controlling the pH, it is then possible to interconvert the protonated monomer into the imidazolate-bridged deprotonated oligomer and *vice versa*. Likewise, in a minor extension, such imidazole-containing complexes have also been used as precursors of heterobimetallic systems.[5,6]

However, examples of the copper(II) co-ordination of imidazolecarboxyaldehydes themselves are scarce, they are limited to only two structural characterised copper(II) complexes,[7,8] having Cu–O(aldehyde) distances of about 2.8 Å. In view of this, we decided to study the co-ordination properties of some imidazolecarboxyaldehydes to copper(II), a magnetically and biologically relevant metal ion. In this paper, we report the synthesis and crystal structure of the complex $[Cu(HL^1)_3](ClO_4)_2$ (HL^1 = 4-methyl-5-imidazolecarboxyaldehyde) and its reactivity with 1,2- and 1,3-diaminopropane to evaluate the viability of the condensation reaction. Likewise, the products obtained from deprotonation, in a basic medium, of the condensation compounds and the precursor $[Cu(HL^1)_3](ClO_4)_2$ itself were studied.

Results and discussion

HL^1 reacts in a neutral medium with $Cu(ClO_4)_2 \cdot 6H_2O$ in 3 : 1 stoichiometry to give the mononuclear complex $[Cu(HL^1)_3](ClO_4)_2$ **1**. The IR spectrum shows the imidazole NH stretching vibration at 3122 cm^{-1} and the characteristic bands due to the ClO_4^- anions centred at 1110 cm^{-1}, thus indicating that the imidazole groups remain protonated. Moreover, two C=O vibrations at 1651 and 1626 cm^{-1} are present in the spectrum, split and shifted to lower wavenumbers with respect to that of the free ligand, at 1676 cm^{-1}, suggesting the existence of two non-equivalent co-ordinated aldehyde groups.

The structure consists of a $[Cu(HL^1)_3]^{2+}$ cation and two perchlorate anions. A perspective view of the mononuclear fragment together with the atom numbering scheme is shown in Fig. 1. Selected bond distances and angles are listed in Table 1. Three ligands are bonded to the copper(II) ion in a bidentate chelate fashion through the imidazole nitrogen and aldehyde oxygen atoms, leading to a CuN_3O_3 chromophore. The co-ordination of each bidentate ligand forms a five-membered chelate ring, exhibiting very significant differences between the Cu–N and Cu–O distances. The co-ordination geometry of the copper(II) can be considered as distorted octahedral, in which

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Table 1 Selected bond lengths (Å) and angles (°) for compound **1**

Cu–N(21)	1.961(10)
Cu–N(1)	1.978(8)
Cu–N(11)	1.984(9)
Cu–O(27)	2.068(8)
Cu–O(7)	2.444(8)
Cu–O(17)	2.453(8)
C(6)–O(7)	1.227(13)
C(16)–O(17)	1.195(13)
C(26)–O(27)	1.202(15)
N(21)–Cu–O(27)	80.9(4)
N(1)–Cu–O(7)	76.1(3)
N(11)–Cu–O(17)	76.5(3)
C(5)–N(1)–Cu	136.7(8)
C(2)–N(1)–Cu	117.4(7)
C(15)–N(11)–Cu	136.9(8)
C(12)–N(11)–Cu	115.7(7)
C(25)–N(21)–Cu	143.2(9)
C(22)–N(21)–Cu	111.7(8)

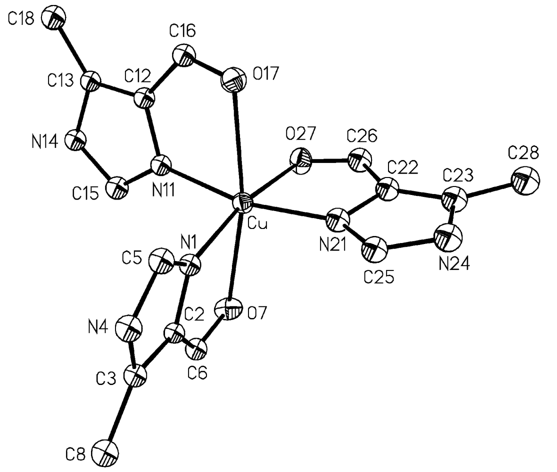


Fig. 1 A perspective view of the cation $[Cu(HL^1)_3]^{2+}$ **1**.

the co-ordination basal plane is defined by three imidazolyl nitrogen atoms, N(1), N(11) and N(21), from the three different ligands and one aldehyde oxygen atom, O(27) belonging to the N(21)-containing ligand, whereas at the apical positions, the remaining two aldehyde oxygen atoms O(7) and O(17) are co-ordinated at longer distances of 2.444(8) and 2.453(8) Å, respectively. Thus, there are two different ligand co-ordination modes, one involving only equatorial positions and another one involving equatorial and axial positions on the copper co-ordination sphere. The copper ion is approximately in the equatorial N_3O plane but the four atoms are not completely coplanar. Thus, the N(1) and N(11) atoms deviate significantly from this plane [0.148(4) and 0.144(4) Å, respectively] toward the corresponding O(7) and O(17) atoms, as another consequence of the small bite of the chelate ligand. The skeleton imidazolyl rings are planar with bond distances and angles that do not merit any particular comment.

As has already been noted, only two structurally characterised imidazolecarboxyaldehyde copper(II) complexes have been reported so far.[7,8] The first one, $[Cu(HL^1)_4](NO_3)_2(H_2O)_2$,[7] exhibits four short Cu–N (imidazole) bonds of about 2 Å, with a flattened tetrahedral geometry. The carbonyl oxygen atoms, however, are located at considerably longer distances (>2.8 Å) from the metal than those found in **1**. In the second one, $[Cu(HL)_2Cl_2]$ (HL is 2-benzylthio-4-formyl-1-*p*-methoxyphenylimidazole),[8] the co-ordination geometry of the copper(II) ion can be considered as square-planar CuN_2Cl_2, with typical bond distances of about 2 Å, whereas the carbonyl oxygen atoms are semico-ordinated at longer distances of 2.71 Å. Hence, these two examples cannot be considered as genuine imidazolecarboxyaldehyde copper(II) complexes involving carbonyl–Cu co-ordination.

Imidazolyl-containing copper(II) complexes have previously been reported as precursors of self-assembly reactions.[4,5,9] This means that, in basic media, the imidazolate nitrogen atom generated co-ordinates the copper(II) ion of an adjacent unit, giving rise to a polymer in which the copper(II) ions are sequentially bridged by imidazolate groups. When complex **1** is dissolved in a KOH-containing methanol solution, a dark blue powder **2** precipitates a few seconds later. This product is insoluble in common solvents and its IR spectrum does not show bands due to either ν(N–H) or ν(Cl–O) stretching vibrations. The elemental analyses agree with the empirical formula $[Cu(L^1)_2]$. Magnetic susceptibility data for **2** were collected on a powdered sample in the 4–290 K range. The $\chi_M T$ product at 290 K is 0.35 $cm^3\ mol^{-1}$ K, which is compatible with the spin-only value for $S = 1/2$. As the temperature is lowered, $\chi_M T$ gradually decreases (Fig. 2), indicating that an antiferromagnetic interaction operates between the copper(II) ions, which is also apparent from the existence of a maximum at about 100 K in the χ_M *vs.* T curve. The magnetic susceptibility data were analysed on the basis of the isotropic spin Hamiltonian $H = -J\Sigma_{i=1}^{n-1} S_i \cdot S_{i+1}$ for one-dimensional infinite chain systems.[10] The best fitting led to $J = -56.4\ cm^{-1}$ and $g = 2.10$.

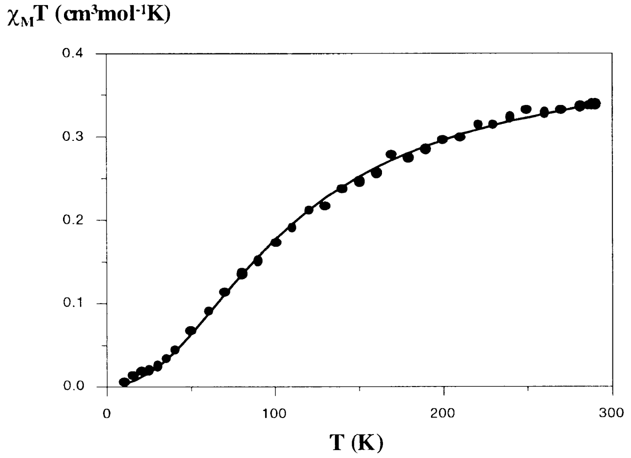


Fig. 2 Temperature dependence of $\chi_M T$ ($cm^3\ mol^{-1}$ K) for $[Cu(L^1)_2]_n$ **2**. Solid lines were generated from the corresponding best-fitting magnetic parameters.

The present J value suggests that an imidazolate group bridges two copper(II) ions at their equatorial positions (J values normally are in the range from -40 to $-100\ cm^{-1}$) rather than at their axial positions (J values ranging from -1 to $-15\ cm^{-1}$).[1,4]

From the analytical, spectroscopic and magnetic data it is reasonable to propose for this complex a polymeric structure formed by $[Cu(L^1)_2]$ units, in which the copper(II) ions are sequentially bridged by imidazolate groups. This means that the self-assembly reaction of **1** induces the removal of one of the three bidentate ligands, which is more likely due to the stronger affinity of the imidazolate nitrogen atom of an adjacent unit for copper(II) compared to the carbonyl oxygen atom. This fact is not surprising, taking into account the long Cu–O(7) and Cu–O(17) bond distances in **1** of about 2.45 Å. Likewise, after ligand removal, an arrangement process would take place, so that the additional and strong co-ordination of the imidazolate atom belonging to an adjacent unit would involve an equatorial and not an axial position on the copper co-ordination polyhedra, in agreement with the magnetic data.

On the other hand, **1** reacts with 1,3-diaminopropane in 1 : 1 stoichiometry to give a blue powder **3**, whose elemental analyses agree with the empirical formula $[Cu(H_2L^2)](ClO_4)_2$, where H_2L^2 is the Schiff-base ligand obtained from the condensation of 4-methyl-5-imidazolecarboxyaldehyde and 1,3-diaminopropane in 2 : 1 stoichiometry (Scheme 1). Its IR spectrum shows the imidazole NH stretching vibration at 3140 cm^{-1} and the characteristic bands due to the ClO_4^- anions at about 1100 cm^{-1}. The presence of the NH band indicates that the 1,3-diaminopropane does not act as a base in this reaction, which would generate the self-assembled complex **2**, but properly as a diamine, so leading to a Schiff-base copper(II) complex formed by the condensation of the carbonyl groups of **1** and the $-NH_2$ groups of the diamine. This means that the co-ordinated carbonyl groups in **1** are able to carry out a condensation reaction with an amine. When the amine is 1,3-diaminopropane, the condensation reaction takes place simultaneously with the removal of one of the three bidentate ligands.

However, when 1,2-diaminopropane was used, no product was isolated. The expected complex $[Cu(H_2L^3)](ClO_4)_2$ **4** (Scheme 1), cannot be prepared by using this method and can only be obtained by direct reaction of copper(II) perchlorate and H_2L^3; this latter prepared by condensation of 4-methyl-5-imidazolecarboxyaldehyde and 1,2-diaminopropane in 2 : 1 stoichiometry (Scheme 1), following the general method we have previously reported.[5,9]

The fact that **4**, unlike **3**, cannot be prepared by direct reaction of **1** and the corresponding diamine must be a consequence of the sterically promoted low reactivity of the $-NH_2$ group close to the methyl in 1,2-diaminopropane, such that the chelate co-ordination does not take place.

The structure of **4** was confirmed by solving the structure by X-ray diffraction methods; it consists of a $[Cu(H_2L^3)]^{2+}$ cation and two perchlorate, one of them semico-ordinated. A perspective view of the mononuclear fragment together with the atom numbering scheme is shown in Fig. 3. Selected bond distances and angles are listed in Table 2. The co-ordination geometry of the copper(II) ion is distorted square-pyramidal, where the co-ordination basal plane is defined by the N_4 donor atoms of the nondeprotonated ligand, with typical Cu–N distances of

Table 2 Selected bond lengths (Å) and angles (°) for compound **4**

Cu–N(10)	1.955(4)
Cu–N(7)	1.965(4)
Cu–N(1)	1.974(4)
Cu–N(13)	1.980(4)
Cu–O(1)	2.363(3)
N(10)–Cu–N(7)	81.02(17)
N(7)–Cu–N(1)	82.45(16)
N(10)–Cu–N(13)	81.88(16)
N(1)–Cu–N(13)	114.04(15)
Cl(1)–O(1)–Cu	122.10(19)
C(2)–N(1)–Cu	109.6(3)
C(5)–N(1)–Cu	143.8(3)
C(12)–N(13)–Cu	110.0(3)
C(14)–N(13)–Cu	143.6(3)

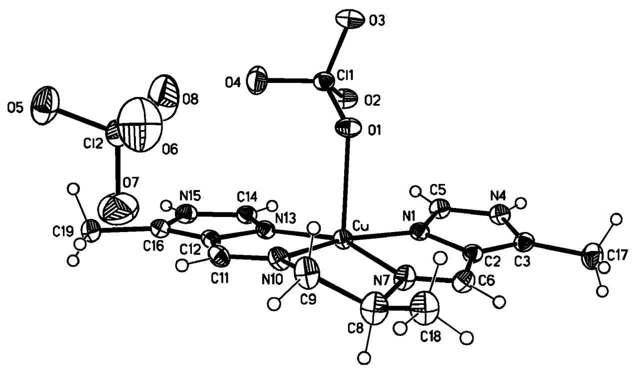
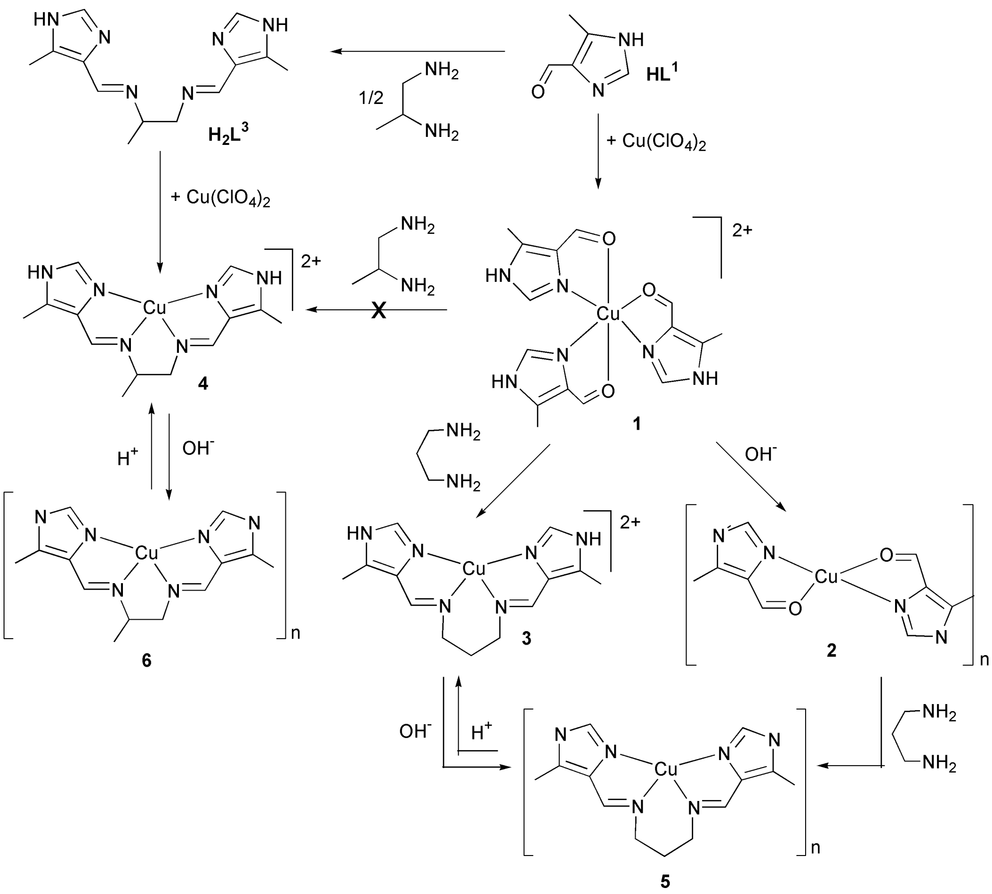


Fig. 3 A perspective view of the complex $[Cu(H_2L^3)(ClO_4)](ClO_4)$ **4**.



Scheme 1

about 1.97 Å. The O(1) atom belonging to one of the perchlorate anions occupies the apical position with a longer bond distance of 2.363(3) Å. The four basal nitrogen atoms are planar while the copper(II) ion deviates 0.143(2) Å from this N_4 plane toward the apical position, as expected for this geometry. The imidazole rings are planar and form dihedral angles with the mean co-ordination basal plane of 9.1(3) and 3.0(3)°, so that the cation $[Cu(H_2L^3)]^{2+}$ is essentially planar.

Both complexes **3** and **4** in basic media have the ability to co-ordinate to another copper(II) ion and simultaneously to receive, at the axial site, the deprotonated imidazolate nitrogen atom of another copper–ligand unit, yielding the respective self-assembled polymers $[Cu(L^2)]_n$ **5** and $[Cu(L^3)]_n$ **6**. The reactions are reversible since, when the polymers **5** and **6** are treated with perchloric acid, the structures are broken, leading to the undeprotonated monomeric complexes **3** and **4**, respectively (Scheme 1). As expected, **5** and **6** are insoluble in common solvents and their IR spectra show no bands due to ν(N–H) and ν(Cl–O) stretching vibrations. We have previously reported similar examples of this kind of self-assembly reactions with similar copper(II) complexes.[5,9] So, taking into account this precedent and the analytical and spectroscopic properties of **5** and **6**, their structure would consist of infinite zigzag chain formed by copper(II)–ligand units, in which the copper(II) ions are sequentially bridged by imidazolate groups, involving the equatorial and axial positions of the respective square-pyramidal co-ordination polyhedra of the copper(II) ions. In fact, the magnetic properties of **5** and **6** are similar to those previously reported for very close self-assembled imidazolate-bridged copper(II) polymers,[5,9] showing a quasi-negligible antiferromagnetic exchange interaction between the copper(II) ions as a result of the fact that the imidazolate bridge involves the axial position of a square-pyramidal polyhedron where the unpaired spin density is very poor.

Finally, it must be noted that **5** can be directly obtained from the condensation reaction of **2** and 1,3-diaminopropane (Scheme 1), which agrees with the existence of co-ordinated aldehyde groups in **2**. However, it is not possible to prepare **6** by reacting **2** and 1,2-diaminopropane. This fact can be again explained by the low reactivity of the $-NH_2$ group close to the methyl substituent in 1,2-diaminopropane.

Experimental

Physical measurements

Elemental analyses were carried out on a Fisons-Carlo Erba analyzer, model EA 1108. IR: Midac prospect FT-IR model (KBr pellets). Variable-temperature magnetic susceptibility data were collected on powdered samples of the compounds with the use of a pendulum type magnetometer (MANICS DSM8) equipped with a helium continuous-flow cryostat working in the 290–4.2 K range and a Drusch EAF 164E electromagnet. Data were corrected for the diamagnetism of the ligands using Pascal's constants.

X-Ray crystallographic study

Single-crystal data collections for **1** and **4** were performed at −80 °C on a Rigaku AFC7S diffractometer using graphite monochromatized Mo-Kα radiation. Both data sets obtained were corrected for Lorentz and polarization effects, and for absorption (ψ scan). The structures were solved by direct methods and refined by full-matrix least squares techniques on F^2 using the SHELX-97 program package.[11] In **1**, one of the two perchlorate ions is disordered, with all atoms occupying two neighbouring positions. Also, in **4**, one of the perchlorate ions is disordered, with each of the oxygen atoms occupying two positions. For **1**, the copper atom, chlorine atoms and fully occupied oxygen atoms were refined with anisotropic displacement parameters. For **4**, non-hydrogen atoms, except disordered oxygen atoms, were refined with anisotropic displacement parameters. For both structures, hydrogen atoms were included in the calculations at fixed distances from their host atoms and treated as riding atoms using the SHELX-97 default parameters. Compound **1** crystallizes in non-centrosymmetric space group. The space group and absolute configuration of **1** was determined by refinement of Flack's x parameter. Crystallographic data for **1** and **4** are listed in Table 3.

Table 3 Crystallographic data for complexes **1** and **4**

	1	**4**
Empirical formula	$C_{15}H_{18}Cl_2CuN_6O_{11}$	$C_{13}H_{18}Cl_2CuN_6O_8$
Formula weight	592.79	520.77
Crystal system	Trigonal	Monoclinic
Space group	$P3_2$ (no. 145)	$P2_1/n$ (no. 14)
a/Å	10.446(2)	12.241(3)
b/Å	10.446(2)	10.048(3)
c/Å	18.561(3)	17.149(5)
β/°		109.35(3)
V/Å^3	1754.0(6)	1990.1(10)
Z	3	4
D_{calc}/g cm^{-3}	1.684	1.738
μ(Mo-Kα)/cm^{-1}	12.31	14.22
Data/parameters	2184/219	3603/271
$R1(F_o)^a$ $[I > 2\sigma(I)]$	0.0634	0.0526
$wR2(F_o^2)^b$ $[I > 2\sigma(I)]$	0.1469	0.1383

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

CCDC reference numbers 168493 and 168494.

See http://www.rsc.org/suppdata/dt/b1/b106982a/ for crystallographic data in CIF or other electronic format.

Preparation of complexes

CAUTION: Perchlorate salts are potentially explosive and only should be handled in small quantities. All reagents were of analytical grade and used without further purification.

$[Cu(HL^1)_3](ClO_4)_2$ 1. A methanolic solution of copper(II) perchlorate hexahydrate (1 mmol, 0.371 g) was slowly added to a solution of 4-methyl-5-imidazolecarboxyaldehyde (3 mmol, 0.330 g) in methanol (40 mL) with continuous stirring. The resulting blue clear solution kept at room temperature for two days provided well-developed blue crystals, which were filtered off and air dried; yield 78%. Anal. calcd for $C_{15}H_{18}N_6O_{11}Cl_2Cu$: C, 30.4; H, 3.0; N, 14.2%. Found: C, 30.4; H, 3.1; N, 14.1%.

$[Cu(L^1)_2]_n$ 2. A methanolic aqueous solution of KOH (1 mmol, 0.056 g) was directly added to 50 mL of a solution of **1** (0.5 mmol, 0.296 g) in methanol/water 4 : 1. A dark blue powder immediately precipitated, which was filtered off, vigorously washed with water, methanol and diethyl ether and air dried; yield 92%. Anal calcd for $C_{10}H_{10}N_4O_2Cu$: C, 42.6; H, 3.6; N, 19.9; Cu, 22.6%. Found: C, 42.6; H, 3.7; N, 19.7; Cu, 22.4%.

$[Cu(H_2L^2)](ClO_4)_2$ 3. To a methanolic solution of **1** (0.5 mmol, 0.296 g), an equimolar amount (0.037 g) of 1,3-diaminopropane was added. The resulting blue solution was stirred for a few minutes and kept at room temperature for one day to develop blue crystals, which were filtered and air dried; yield 76%. Anal calcd for $C_{13}H_{18}N_6O_8Cl_2Cu$: C, 30.0; H, 3.5; N, 16.1%. Found: C, 29.9; H, 3.5; N, 16.0%.

$[Cu(H_2L^3)(H_2O)](ClO_4)_2$ 4. Compound **4** was prepared using the same procedure as for **3**, but with 1,2-diaminopropane, giving a green oil, from which no pure material could be isolated. Thus, the complex was prepared by direct reaction from the ligand and copper(II) perchlorate hexahydrate following a procedure we have previously reported.[5,9]

$[Cu(L^2)]_n$ 5. A methanolic aqueous solution of KOH (1 mmol, 0.056 mg) was directly added to 50 mL of a solution of **3** (0.5 mmol, 0.260 g) in methanol. A green powder immediately precipitated, which was filtered off, carefully washed with water, methanol and diethyl ether and air dried; yield 92%. Anal calcd for $C_{13}H_{16}N_6Cu$: C, 48.8; H, 5.0; N, 26.3; Cu, 19.9%. Found: C, 48.9; H, 5.0; N, 26.2; Cu, 20.0%.

$[Cu(L^3)]_n$ 6. This complex can be prepared following the same procedure described for **5**, by starting from **4** instead of **3**. Anal calcd for $C_{13}H_{16}N_6Cu$: C, 48.8; H, 5.0; N, 26.3; Cu, 19.9%. Found: C, 48.8; H, 5.1; N, 26.2; Cu, 19.9%.

On the other hand, addition of perchloric acid to a water suspension of **4** or **6** until the precipitate dissolves gives rise to blue solutions, from which the complexes **3** or **5** are obtained, respectively.

Likewise, complex **5** can be obtained by reacting **2** and 1,3-diaminopropane in 1 : 1 stoichiometry at 50 °C in methanol after 10 min of stirring. When 1,2-diaminopropane was used, no pure material could be isolated.

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