Maleamate(−1) and Maleate(−2) Copper(II)−2,2′-Bipyridine Complexes: Synthesis, Reactivity and Structural and Physical Studies


Keywords: Amides / Hydrolysis / Copper / Magnetic properties

A systematic investigation of the 1:2:1 2Cu(NO3)2·2H2O/H2L/bpy/LiOH/H2O reaction system in MeCN/H2O was carried out. The compounds [Cu2(HL)2(bpy)2][NO3]2·2H2O (I), [Cu2(L2)2(bpy)2][NO3]2·2H2O (I-2H2O), [Cu2(L2)2(bpy)2][NO3]2·2H2O (II-2H2O), [Cu3(L2)2(bpy)2][NO3]2·2H2O (III-2H2O) and [Cu2(L)4][NO3]2·2nH2O (IV-2nH2O) were isolated, depending on the crystallization method employed. Complexes 1, 2, 2H2O and 4·2nH2O contain the maleate(−2) anion (L-2), which was formed in situ through metal-ion-assisted hydrolysis of the primary amide group of H2L. Efforts to prepare complex 3 from the direct use of maleic acid (H2L) afforded compounds 4·2nH2O, [Cu4(L2)2(F2)(bpy)2][NO3]2·2H2O and [Cu2(L)4][NO3]2·2H2O (IV-2H2O) and [Cu(NO3)2(bpy)-(H2O)5][NO3] (6) from the 1:1:1:2 Cu(NO3)2·2H2O/H2L/bpy/LiOH-H2O reaction system in MeCN/H2O. The maleamate(−1) ligand presents the less common η1:η2 coordination mode in the cations of 1, 1·2H2O and 2. The maleate(−2) ligand exhibits the η1:η1:η1:η3 coordination mode in the [Cu4L2]2+ cations of 3·2H2O and 5·4H2O and in the [Cu2L2F2]2+ heterometallic cation of 2. The crystal structures of the complexes are stabilized by various H-bonding patterns. Characteristic IR bands of the complexes are discussed in terms of the known structures and the coordination modes of the ligands. Magnetic susceptibility measurements for 3·2H2O reveal weak ferromagnetic interactions along the periphery of the Cu4 rhombus (J = 3.3 cm−1, −2J1S1S1 Hamiltonian formalism), which stabilizes an S = 2 ground state.

© 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2009

Introduction

Metal carboxylates represent a fruitful source for molecular clusters[8] and coordination polymers,[3] whose aesthetic beauty and structural complexity is closely related to their physical properties. Outstanding in the field are the α,ω-dicarboxylate ligands, because (i) the presence of the two carboxylato moieties, (ii) the relative orientation of the two carboxylato groups, (iii) the mono- or dianionic forms, (iv) the possibility of various coordination modes, and (v) their ability to form secondary building blocks enhancing the construction of novel multidimensional architectures.[3] The conformational flexibility (for n ≥ 1 in I, Scheme 1) or the π-induced rigidity of the carbon atom (see Scheme 1-IV, Scheme 1) offer additional variables that can influence the structural characteristics of the metal complexes. Moreover, the combination of the α,ω-dicarboxylates, such as I-IV in Scheme 1, with aromatic bidentate N,N'-chelates (e.g. 2,2′-bipyridine, 1,10-phenanthroline) has led to a variety of structures.[4]

On the other hand, the coordination chemistry of the monoamides of the aliphatic α,ω-dicarboxylates has been scarcely investigated [e.g. −OOC-(CH2)n-CONH2, VI, n = 2,3,4,5,...]. −OOC-CH=CH-CONH2, VI, fumarate monoamide; VII maleate monoamide or maleamate; −OOC-C=CCONH2, VIII, acetylene dicarboxylate monoamide; Scheme 1]. These types of ligands are expected to yield metal complexes with different chemical and structural features than those of the α,ω-dicarboxylates, because of the different charge, electronic properties and hydrogen bonding ability of the amide group.

Keeping these in mind, we have embarked in a research programme aiming at the investigation of the coordination chemistry of the monoamides of aliphatic α,ω-dicarboxylates in the presence of aromatic bidentate N,N'- or tridentate N,N',N'-chelates. Our efforts have yielded metal complexes that exhibit a variety of structural features, as far as lability and dimensionality are concerned, because of the coordination versatility of the carboxylato group and the hydrogen bonding ability of the amide group. We have explored ligand systems involving the succinamidate(−1) (n = 2 in V of Scheme 1, Hucm) and the maleamate(−1) (VII in Scheme 1, HL-) ligands[6] in combination with aromatic bidentate N,N'- or tridentate N,N',N'-chelates. We have examined the influence of various synthetic parameters, such as the reaction solvent, the presence or absence of external...
Syntheses of the Complexes

Our previous investigation of the tertiary CuX2·2H2O/ H2L/phen (X = Cl, NO3, ClO4) and Cu(ClO4)2·6H2O/ H2L/bpy reaction systems[6b,6c] led to interesting results concerning the chemical and structural properties of the compounds isolated. In order to examine the extent to which the nature of the inorganic anion of copper(II) might affect the identity of the products from the bpy-containing reaction system, we have expanded our research to the use of Cu(NO3)2·2.5H2O.

Our initial efforts involved the reaction of Cu(NO3)2· 2.5H2O with 2 equiv. H2L and 1 equiv. bpy in the presence of 2 equiv. LiOH·H2O in MeCN/H2O (10:1 v/v). We isolated five different products from the same reaction mixture, depending on the crystallization method employed: (i) layering of the resultant blue solution with a mixture of Et2O/ n-hexane afforded blue prismatic crystals of [Cu2(HL)2(bpy)2(H2O)2](NO3)2 (1·2H2O), (ii) vapour diffusion of the reaction solution with Et2O gave a mixture of blue prismatic crystals of 1·2H2O and dark blue needlelike crystals of [Cu2Li2(L)2(bpy)2(H2O)6][Cu2(L)2(bpy)2(H2O)2](NO3)4 (2) in an approximate 1:1 ratio, (iii) slow evaporation of the reaction solution at room temperature afforded blue crystals of [Cu2(L)2(bpy)2(H2O)2](NO3)2 (1), (iv) storage at ca. 4 °C gave [Cu2(L)2(NO3)2(bpy)2(H2O)2](NO3)2·2H2O (3·2H2O), and (v) storage of the reaction solution in closed vials at room temperature afforded the known complex[7] [Cu(L)2(bpy)2]2nH2O·4·2nH2O (Scheme 2).

Compounds 1 and 1·2H2O contain the same dinuclear cation; the presence of two water solvate molecules in the structure of the latter leads to a completely different crystal structure as a result of hydrogen-bonding interactions.

Complex 2 is quite impressive because it consists of two cationic complexes, one of which contains the maleamate(–1) ligand (HL–, VII in Scheme 1) and is analogous to the cation of 1·2H2O and a second that contains the maleate(–2) ligand (L2–, III in Scheme 1); the latter ligand is also present in complex 3. The dianion of L2– in 2 and 3 was formed in situ by the hydrolysis of the primary amide group of H2L to the carboxylate function. It is well known that such hydrolysis reactions are accelerated by metal ions[8]

We believe that the little amount of water added in the reaction mixture – in order to dissolve LiOH·H2O and to prevent contamination of the product by LiNO3, which is insoluble in anhydrous MeCN – or contained in the starting materials is beneficial to the hydrolysis of the primary amide group and the to the formation of the maleate(–2) ligand followed by its subsequent coordination, which affords 2 and 3·2H2O. The CuII-assisted/promoted HL → L2– transformation was also observed in the case of the Cu(ClO4)2·6H2O/H2L/bpy/OH– reaction system.[6d]

In all cases above, the reaction mixture was gently heated before the crystallization process. By avoiding heating, pure 1·2H2O was obtained from the 1:2:1:2 Cu(NO3)2·2.5H2O/ H2L/bpy/LiOH·H2O reaction mixture, i.e. the compounds 2, 3·2H2O and 3·2nH2O, which contain the maleate(–2) ligand, were not isolated. Without any mechanistic implications, we assume that the gentle heating of the reaction mixture, along with the simultaneous presence of CuII ions, may have facilitated the HL– → L2– transformation.
In order to prepare pure \(3 \cdot 2\text{H}_2\text{O}\) in a rational manner, we used the known complex \([\text{Cu}_2(\text{L}^{-2})\text{(bpy)}_2\text{MeOH}] \cdot 2\text{MeOH}\) (which includes the maleate(-2) dianion) as starting material; its reaction with 2 equiv. \(\text{Cu(NO}_3\text{)}_2 \cdot 2.5\text{H}_2\text{O}\) and 2 equiv. bpy in MeOH affords pure \(3 \cdot 2\text{H}_2\text{O}\).

In a next step, we wondered whether the direct use of \(\text{H}_2\text{L}^{-2}\) might lead to the isolation of \(3\), and we employed the reaction of \(\text{Cu(NO}_3\text{)}_2 \cdot 2.5\text{H}_2\text{O}\) with 1 equiv. \(\text{H}_2\text{L}^{-2}\) and 1 equiv. bpy in the presence of 2 equiv. LiOH \(\cdot \text{H}_2\text{O}\) in MeCN/H\(_2\text{O}\). Three different compounds were isolated from the same light blue reaction solution, depending on the crystallization method employed: (i) layering of the reaction solution with a mixture of Et\(_2\text{O}\)/n-hexane afforded a mixture of blue crystals of \([\text{Cu}_4(\text{L}^{-2})\text{(bpy)}_2(\text{H}_2\text{O})_2\cdot(\text{NO}_3)_2\cdot2(\text{Li(NO}_3\text{)(H}_2\text{O})_3)(\text{NO}_3)_2\cdot2\text{H}_2\text{O}] \cdot 2(\text{NO}_3\cdot2(\text{H}_2\text{O})_2\cdot2\text{H}_2\text{O})\) and light blugreenish platelike crystals of the known \([\text{Cu}^{-}\text{(bpy)}\text{(H}_2\text{O})_3\text{(NO}_3\text{)}_2}\) in an approximate 1:1 ratio, and (ii) storage of the reaction solution in closed vials at ca. 4 °C gave the known compound \([\text{CuL}^{-2}\text{(bpy)}\text{nH}_2\text{O}] \cdot 2\text{nH}_2\text{O}\) (4·2\(\text{nH}_2\text{O}\)).

Complex 5 is quite impressive because it contains a tetranuclear cation, analogous to that of 3 and neutral Li\(^+\) complex molecules.

The isolation of five different compounds, i.e. 1, 1·2\(\text{H}_2\text{O}\), 2, 3·2\(\text{H}_2\text{O}\) and 4·2\(\text{nH}_2\text{O}\), from the \(\text{Cu(NO}_3\text{)}_2 \cdot 2.5\text{H}_2\text{O}/\text{bpy}/\text{LiOH}/\text{H}_2\text{O}\) reaction mixture in MeCN/H\(_2\text{O}\), under different crystallization conditions, constitutes an excellent example of rich coordination chemistry. In addition, the isolation of three different compounds comprising various species, i.e. a Cu\(^{II}\)\(_4\) cation and two neutral Li\(^+\) complex molecules in 5, a 1D complex (4·2\(\text{nH}_2\text{O}\)) and a mononuclear maleate-free complex (6) from the \(\text{Cu(NO}_3\text{)}_2 \cdot 2.5\text{H}_2\text{O}/\text{bpy}/\text{LiOH}/\text{H}_2\text{O}\) reaction mixture in MeCN/H\(_2\text{O}\) by different crystallization conditions is also remarkable. It is well known that solutions of transition-metal ions and one or more ligands can give complicated mixtures of products in equilibrium – as a result of the labile nature of the metal–ligand bonds and other noncovalent bonds that may eventually form (H bonds, π–π stacking etc); the case is further complicated when metal-ion-assisted ligand transformations and/or other reactivity processes also take place. From this multitude of products, it is often possible to isolate one or more compounds by their selective precipitation and subsequent crystallization, although it still remains a challenge to isolate different species from the same reaction mixture, and more so to structurally characterize them.

We came across an analogous behaviour during the investigation of the \(\text{CuCl}_2/\text{H}_2\text{mal}/\text{phen}/\text{LiOH}\cdot\text{H}_2\text{O}\) reaction system in MeOH (H\(_2\text{mal} = \text{malonic acid}\)) from which seven different products were isolated on the basis of their different solubility. The present reaction system involving \(\text{H}_2\text{L}^{-2}\) is much more complicated and interesting, since the observed Cu\(^{II}\)-assisted \(\text{HL}^{-} \rightarrow \text{L}^{-2}\) transformation simultaneously yields ligands with different coordination and electronic properties; the coordination properties of the ligands is reflected by the isolation of species common in both reaction systems examined; thus complex 4·2\(\text{nH}_2\text{O}\) was isolated from both \(\text{HL}^{-}\)- and \(\text{L}^{-2}\)-containing reaction systems, while the Cu\(^{II}\)\(_4\) cation present in 3 and 5 was obtained from \(\text{HL}^{-}\) and \(\text{L}^{-2}\)-containing reaction systems, respectively. Both reaction systems represent excellent examples of dynamic mixtures of various species in equilibrium, from which we were able to isolate a multitude of products on the basis of their selective crystallization.

### Description of the Structures

The molecular structures of the dinuclear cations that are present in complexes 1 and 1·2\(\text{H}_2\text{O}\) are very similar. We give below a comparative structural description for the cations of 1 (Figure 1) and 1·2\(\text{H}_2\text{O}\) (Figure S1). The structure of the cation in both complexes consists of two centrosym-
Maleamate(−1)/Maleate(−2) Copper(II)–2,2′-Bipyridine Complexes

metrically related CuII ions bridged by the carboxylate groups of two HL− ligands that present the less common \( \eta^1: \mu_2 \) coordination mode \( [\text{Cu}1⋅⋅⋅\text{Cu}1′ = 3.346(3) \text{ and } 3.369(5) \text{ Å in } 1 \text{ and } 1\cdot2\text{H}_2\text{O}, \text{ respectively}] \). A chelating bpy and a water molecule complete the five-coordination around each CuII atom. The neutral primary amide groups of the HL− ligands remain uncoordinated. The Cu−O2 distance of 2.861(3) Å in 1 (dashed line in Figure 1) provides evidence for a weak interaction, as has sometimes\(^{[12]} \) (but not always\(^{[13]} \)) been observed for monatomic bridging carboxylate groups. The coordination geometry about each metal ion in both complexes is well described as square pyramidal, in which the bridging carboxylic oxygen atoms occupy the apical positions for the two CuII centres; for example, in 1, atoms O1 and O1′ occupy the apical positions for Cu1 and Cu1′, respectively. Analysis of the shape-determining angles by using the approach of Reedijk, Addison and co-workers\(^{[14]} \) yields values for the trigonality index, \( \tau \), of 0.17 and 0.21 for the CuII ions in 1 and 1⋅2H2O, respectively. The Cu−N and Cu−O bond lengths are in the range 1.960(2)−2.310(2) Å in 1 and 1.966(3)−2.351(3) Å in 1⋅2H2O (Table S1). As expected, the axial bonds are the longest. The structures of the cations of 1 and 1⋅2H2O are quite similar to the structures of the cations in \[\text{[Cu}_2(\text{LH})_2(\text{bpy})_2(\text{H}_2\text{O})_2]\](ClO4)_2 and \[\text{[Cu}_2(\text{LH})_2(\text{bpy})_2(\text{H}_2\text{O})_2]\](ClO4)_2⋅2H2O, previously reported by us.\(^{[6c]} \)

In the crystal lattice of 1, intermolecular hydrogen-bonding interactions are observed, which form a 2D network parallel to the (100) plane (Figure 2, Table S5). In the crystal lattice of 1⋅2H2O, intra- \([\text{O3}−\cdot\cdot\cdot\text{Ow1}]\) and intermolecular hydrogen-bonding interactions \([\text{N3}−\cdot\cdot\cdot\text{O3} (−x, −y, z)]\) form 1D chains parallel to the \( b \) axis, which are further associated and form a 2D network extending parallel to the (001) plane (Figure 3, Table S5).

The structure of complex 2 consists of heterometallic tetranuclear cations \([\text{Cu}_2\text{Li}_2(\text{L})_2(\text{bpy})_2(\text{H}_2\text{O})_6]\)^{2+} (Figure 4), dinuclear cations \([\text{Cu}_3(\text{HL})_2(\text{bpy})_2(\text{H}_2\text{O})_2]\)^{2+} similar to those present in complexes 1 and 1⋅2H2O (Figure 1), and nitrate counterions; the latter two will not be discussed further.

![Figure 1](image1.png) Partially labelled plot of the cation of 1 with ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity. Primed atoms are generated by the symmetry operation \( 1−x, 1−y, −z \).

![Figure 2](image2.png) A part of the 2D structure of 1 showing the H-bonding interactions. Colour code: Cu, black; O, medium grey; N, large white; C, small white. H bonds are presented by dashed lines. Only the N atoms of the bpy ligands are shown.

![Figure 3](image3.png) A part of the 2D structure of 1⋅2H2O showing the H-bonding interactions. Colour code: Cu, black; O, medium grey; N, large white; C, small white. H bonds are presented by dashed lines. Only the N atoms of the bpy ligands are shown.

![Figure 4](image4.png) Partially labelled plot of the Cu^{II}_2Li^{II}_2 cation of 2 with ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity. Primed atoms are generated by the symmetry operation \( −x, −y, 1−z \).
The molecular structure of the heterometallic cation consists of a centrosymmetric cyclic Cu$^{II}$Li$I_{2}$ unit; the metal ions are held together through two η$^{1}$-η$^{1}$-η$^{1}$-μ$^{3}$ L$^{2-}$ ligands. The coordination geometry around each Cu$^{II}$ ion is square pyramidal ($τ = 0.14$). The basal positions of the square pyramid are occupied by the nitrogen atoms of a bpy molecule and atoms O1 and O3 of the L$^{2-}$ ligand, while the apical position is occupied by a coordinated H$_2$O molecule. The Cu–N and Cu–O bond lengths are in the range 1.916(3)–2.275(4) Å (Table S2). The coordination geometry around each Li$^{I}$ ion is tetrahedral and comprises the oxygen atoms O4 and O2 belonging to two L$^{2-}$ ligands and two coordinated H$_2$O molecules [Li–O 1.914(8)–1.967(9) Å]. The structure of the heterometallic tetranuclear cation [Cu$_2$Li$_2$(L'/H$_{11032}$)$_2$(bpy)$_2$(H$_2$O)$_6$]$^{2+}$ is similar to the structure of the neutral complex [Cu$_2$Li$_2$Cl$_2$(mal)$_2$(phen)$_2$(MeOH)$_4$][11] {mal$_2^-$ = malonate($-$2) ligand}.

In the lattice structure of 2, the Cu$^{II}$Li$I_{2}$ cations are hydrogen bonded and form 1D chains, which are further hydrogen bonded to the Cu$^{II}$ cations and the nitrate anions to form a 2D network extending parallel to the (1-10) plane (Figure 5, Table S5).

The structure of complex 3·2H$_2$O consists of tetranuclear cations [Cu$_4$(L'/H$_{11032}$)$_2$(bpy)$_4$(H$_2$O)$_2$]$^{2+}$, NO$_3^-$ counterions and solvate H$_2$O molecules; the latter two will not be further discussed. Each L$^{2-}$ ligand adopts the η$^{1}$-η$^{1}$-η$^{1}$-μ$_3$ coordination mode, thus bridging three Cu$^{II}$ ions of the tetranuclear cation through the formation of a remarkable seven-membered Cu–O carboxylate–C–C=C–C–O carboxylate chelating ring (Figure 6). A chelating bpy, an aqua ligand for both Cu1 and Cu3, and a monodentate nitrate anion for both Cu2 and Cu4, respectively, complete the pentacoordination around each metal ion, thus defining a square pyramidal geometry in which the aqua and the nitrate ligands occupy the apical position for Cu1/Cu3 and Cu2/Cu4, respectively. The Cu–N and Cu–O bond lengths are in the range 1.938(3)–2.308(4) Å (Table S3).

In the crystal lattice of 3·2H$_2$O, the presence of intermolecular hydrogen-bonding interactions between the tetranuclear cations, the nitrates and the solvate H$_2$O molecules result in the formation of a 3D network (Figure 7, Table S5).

The structure of complex 5·4H$_2$O consists of centrosymmetric tetranuclear cations [Cu$_4$(L'/H$_{11032}$)$_2$(bpy)$_4$(H$_2$O)$_2$]$^{2+}$ analogous to those present in complex 3·2H$_2$O, two neutral [Li(NO$_3$)(H$_2$O)$_3$] complexes (Figure 8), NO$_3^-$ counterions and H$_2$O solvate molecules. The Cu–N and Cu–O bond lengths in the [Cu$_4$] cation are in the range 1.954(3)–2.278(4) Å (Table S4). The coordination geometry around the Li$^{I}$ ion is tetrahedral and comprises three aqua ligands and a monodentate nitrate group [Li–O 1.921(10)–2.007(10) Å].
and \(5\cdot4\text{H}_2\text{O}\), the bands at ca. 1445 and 1315 cm\(^{-1}\) are assigned\(^{[17]}\) to the \(v_\beta(B_2)\) [\(v_{\text{as}}(\text{NO}_3)\)] and \(v_\gamma(A_1)\) [\(v_{\text{as}}(\text{NO}_3)\)] bands, respectively; the small difference (ca. 130 cm\(^{-1}\)) in the position of the bands is consistent with the presence of monodentate coordinated \(\text{NO}_3^-\) groups of \(C_{2v}\) symmetry in these compounds.\(^{[17]}\) Complexes \(3\cdot2\text{H}_2\text{O}\) and \(5\cdot4\text{H}_2\text{O}\) have uncoordinated ionic nitrates as counterions as well as coordinated \(\text{NO}_3^-\) groups. As a result, in the spectra of these compounds, there are bands that can be attributed to both groups.

The typical bands of the neutral amide group, i.e. \(v_{\text{as}}(\text{NH}_2)\), \(v_{\text{as}}(\text{NH}_2)\), \(v(\text{C}=\text{O})\) and \(v(\text{CN})\), in the spectra of \(1, 1\cdot2\text{H}_2\text{O}\) and \(2\) (Table S6) are located at almost the same wavenumber as those in the spectrum of Na(HL), which confirms the crystallographically established nonparticipation of the amide group in coordination. The difference \(\Delta\), where \(\Delta = v_{\text{as}}(\text{CO}_2) - v_{\text{as}}(\text{CO}_2)\), for \(1\) (221 cm\(^{-1}\)), \(1\cdot2\text{H}_2\text{O}\) (219 cm\(^{-1}\)) and \(2\) (220 cm\(^{-1}\)) is more than that of Na(HL), as expected for the crystallographically confirmed, essentially monatomic bridging mode of the carboxylate ligation.\(^{[5,18]}\)

The difference \(\Delta\) for \(3\cdot2\text{H}_2\text{O}\) (116 cm\(^{-1}\)) and \(5\cdot4\text{H}_2\text{O}\) (112 cm\(^{-1}\)) is much smaller than that of the "free" maleate(–2) ion (200 cm\(^{-1}\))\(^{[7a]}\) (Table S7), as expected for the bidentate bridging mode of the carboxylate ligation.\(^{[18]}\) Owing to the presence of two different ligands (L\(^{2-}\), HL\(^-\)) in \(2\), two \(v_{\text{as}}(\text{CO}_2)\) and two \(v_{\text{as}}(\text{CO}_2)\) bands appear in its spectrum. The pair at 1589/1414 cm\(^{-1}\) (\(\Delta = 175\) cm\(^{-1}\)) is attributed to the bidentate bridging carboxylate groups of the L\(^{2-}\)-ligand, while the pair at 1603/1383 cm\(^{-1}\) (\(\Delta = 220\) cm\(^{-1}\)) to the monatomic bridging carboxylate groups of HL\(^-\).\(^{[18]}\)

Magnetic Studies

The \(\chi_MT\) product for \(3\cdot2\text{H}_2\text{O}\) (0.5 T) is 1.65 cm\(^3\)mol\(^{-1}\)K, in agreement with the value predicted for four noninteracting \(S = 1/2\) ions (\(g = 2.1\)). Upon cooling, this value increases continuously up to a value of 3.03 cm\(^3\)mol\(^{-1}\)K at \(2\) K (Figure 10), which is in agreement with an \(S = 2\) ground state. The overall behaviour indicates ferromagnetic interactions, albeit weak.

The symmetry of \(3\cdot2\text{H}_2\text{O}\), as revealed by its molecular structure (Figure 6), allows us to consider one coupling parameter for all exchange interactions between adjacent Cu\(^{\text{II}}\) ions along the periphery of the rhombus. Diagonal interactions were neglected because of the large Cu···Cu distances [Cu2···Cu4 7.27 Å] and/or because of the fact that possible exchange would have to be through-space and transmitted through nonmagnetic orbitals [in the case of Cu1 and Cu3]. Thus, the spin Hamiltonian used was as shown.

\[
H = -2J(S_iS_j + S_iS_k + S_jS_i + S_kS_i)
\]

Fits performed on the basis of this model yield excellent results. Best-fit parameters are \(J = +3.3\) cm\(^{-1}\), \(g = 2.123\) and \(R = 7.8 \times 10^{-5}\). Simulations of \(M\) vs. \(H\) data at 2 K (Figure 10, inset) based on the best-fit solution (by considering \(g = 2.197\)) or a Brillouin curve (\(S = 2\), \(g = 2.197\)) were practically superimposable. However, at 5 K, where excited
The use of the $L^2$/bpy “ligand blend” in reactions with Cu(NO$_3$)$_2$·2.5H$_2$O – in order to prepare 3·2H$_2$O in a rational manner – yielded the new complex 5·4H$_2$O and the known complexes 4·2nH$_2$O$^{[3]}$ and 6.$[9]$ As in the HL$^-$ reaction system, the three complexes have been isolated from the same reaction solution, either as mixtures or in the pure form, depending on their different solubilities. Complex 5·4H$_2$O contains a tetraneuclear cation that is structurally similar to that present in 3·2H$_2$O and neutral tetrahedral Li$^+$ complexes. The chemistry of the Cu(NO$_3$)$_2$·2.5H$_2$O/ L$^2$-/bpy system shows similarities and differences to that of the corresponding Cu(ClO$_4$)$_2$·6H$_2$O/L$^2$-/bpy system.$^{[6,8]}$ The common feature is the isolation of the 1D complex 4·2nH$_2$O. The ClO$_4^-$-containing system afforded the 1D complex [Cu$_2$(L$'$)(bpy)$_2$(H$_2$O)$_2$(ClO$_4$)$_2$]$_n$ and the dinuclear complex [Cu$_2$(L$'$)$_2$(bpy)$_2$], while the replacement of ClO$_4^-$ with NO$_3^-$ yielded the tetraneuclear complex 5·4H$_2$O, in which the coordination of the nitrates blocks further polymerization. The L$^2$- ligand in the structures of 2, 3/5 and 4 adopts three different coordination modes, a fact that is indicative of its coordination versatility and capability of affording various structural architectures.

The rich coordination chemistry of HL$^-$ and the metal-assisted hydrolysis and methanolysis$^{[6]}$ of the primary amide group to the carboxylate function and the monomethyl ester, respectively [leading to the in situ formation of maleamate(–2) and monomethyl maleate(–1) ligands, respectively], that have been observed during the investigation of the CuX$_2$·2nH$_2$O (X = Cl$^-$, ClO$_4^-$, NO$_3^-$)/H$_2$L/N, N'-chelate reaction systems has prompted us to investigate analogous reaction mixtures with mono- and tridentate chelating ligands; our results will be reported soon.

Concluding Comments and Perspectives

The use of the HL/bpy “ligand blend” in reactions with Cu(NO$_3$)$_2$·2.5H$_2$O yielded dinuclear, tetraneuclear and polymeric complexes, i.e. the new complexes 1, 2·2H$_2$O, 2 and 3·2H$_2$O and the known$^{[3]}$ complex 4·2nH$_2$O.$^{[9]}$ The chemistry of the Cu(NO$_3$)$_2$·2.5H$_2$O/HL/bpy system shows similarities and differences to that of the corresponding Cu(ClO$_4$)$_2$·6H$_2$O/HL/bpy system.$^{[6,8]}$ Complexes containing the cation [Cu$_2$(HL)$_2$(bpy)$_2$(H$_2$O)$_2$]$^{2+}$ (1 and 2·2H$_2$O) have been isolated from both reaction systems, as well as the 1D coordination polymer [Cu$_2$(L$'$)(bpy)$_2$(H$_2$O)$_2$]$_n$-2nH$_2$O (4·2nH$_2$O). L$^2$- is the maleate(–2) ligand that was formed in situ through the Cu$^{II}$-assisted HL$^-$ → L$^2$- transformation. The replacement of ClO$_4^-$ with the coordinatively active NO$_3^-$ additionally afforded complex 2, which contains both HL$^-$ and L$^2$- ligands, and the tetraneuclear complex 3·2H$_2$O, which contains exclusively L$^2$- ligands. All five compounds have been isolated from the same reaction solution, either as mixtures or in the pure form, depending on the crystallization method employed. Thus, the reaction system under investigation constitutes a dynamic mixture of species, whose crystallization and subsequent isolation is based on their different solubilities.

Experimental Section

General Procedures and Materials: All manipulations were performed under aerobic conditions by using materials as received (Aldrich Co). All chemicals and solvents were of reagent grade. Elemental analyses for C, H and N were performed on a Perkin–Elmer 2400 II automatic analyzer. IR spectra were recorded from KBr pellets in the range 4000–400 cm$^{-1}$ on a Bruker Equinox 55/S FTIR spectrophotometer. [Cu$_2$(L$'$)$_2$(bpy)$_2$]·2MeOH was prepared as previously reported.$^{[8]}$ Variable-temperature magnetic susceptibility measurements were carried out on a polycrystalline sample of 3·2H$_2$O in the temperature range 2.0–300 K by using a Quantum Design MPMS SQUID magnetometer under magnetic fields of 0.5, 1.0 and 1.5 T. Diamagnetic corrections for the complexes were estimated from Pascal’s constants. The magnetic susceptibility was computed by exact calculation of the energy levels associated with the spin Hamiltonian, through diagonalization of the full-matrix with a general-symmetry program.$^{[39]}$ Least-squares fittings were accomplished with an adapted version of the function-minimization program MINUIT.$^{[20]}$ The error factor R is defined as $R = \sqrt{\sum(x_{\text{exp}} - x_{\text{cal}})^2/N(x_{\text{exp}})}$, where $N$ is the number of experimental points. Simulations of the magnetization $M$ vs. applied field $H$ were carried out with the MAGPACK program package, with parameters derived from fits of the magnetic susceptibility.$^{[21]}$
Preparation of \([\text{Cu}_2(\text{HL})_2(\text{bpy})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2]2\text{H}_2\text{O} (1\cdot\text{2H}_2\text{O})\), \([\text{Cu}_2(\text{LiL}(\text{L}'))_2(\text{bpy})_2(\text{H}_2\text{O})_2(\text{H}_2\text{O})_3]\text{NO}_3\) (2): A colourless aqueous solution (2 mL) of LiOH·H_2O (0.018 g, 0.43 mmol) was added to a colourless solution of H_2L (0.050 g, 0.43 mmol) in MeCN (20 mL) to give a white suspension, which was stirred under heating for 50 min. Solid bpy (0.034 g, 0.22 mmol) was added, and the solution was stirred under heating for 1 h. A turquoise solution of Cu(NO_3)_2·2H_2O (0.051 g, 0.22 mmol) in MeCN (10 mL) was then added to give a blue suspension, which was filtered off to obtain a final blue solution. X-ray quality, blue prismatic crystals of 1·2H_2O were formed by layering of the blue solution with a mixture of EtO/MeCN/hexane (10 mL, 1:1 v/v). The crystals were collected by filtration under vacuum, washed with cold MeCN (2 mL) and EtO (3 mL) and dried in air. Yield: 0.10 g (ca. 55 %). FTIR for 1·2H_2O (KBr pellet): \(\nu = 3427\) (s br.), 3127 (s br.), 2925 (s br.), 2364 (m), 1683 (m), 1579 (s), 1523 (m), 1312 (s), 1290 (m), 1263 (m), 1132 (s), 1096 (m), 1030 (m), 983 (s), 891 (m), 725 (m), 678 (w), 612 (w) cm\(^{-1}\). 

Vapour diffusion of EtO onto the final blue solution of the reaction afforded blue prismatic crystals and needlelike dark blue crystals in an approximate ratio of 1:1, which were separated manually and dried in air. X-ray crystallography revealed that the blue prisms correspond to complex 1·2H_2O (see above) and the dark blue needlelike crystals correspond to the known complex \([\text{Cu}_2(\text{HL})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2]2\text{H}_2\text{O} (\text{3·2H}_2\text{O})\).

Preparation of \([\text{Cu}(\text{HL})(\text{bpy})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2]2\text{H}_2\text{O}\), \([\text{Cu}(\text{L})(\text{bpy})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2]\text{Li}_2\text{O}\) (3·2H_2O) (3·2H_2O): FTIR for \([\text{Cu}(\text{HL})(\text{bpy})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2]2\text{H}_2\text{O}\) (KBr pellet): \(\nu = 3421\) (s br.), 3108 (w), 2925 (s br.), 2364 (m), 1683 (m), 1579 (s), 1523 (m), 1312 (s), 1290 (m), 1263 (m), 1132 (s), 1096 (m), 1030 (m), 983 (s), 891 (m), 725 (m), 678 (w), 612 (w) cm\(^{-1}\). 


eurjc.org
Light blue needlelike crystals were formed upon standing of the final light blue solution in a closed vial at ca. 4°C. The crystals were collected by filtration under vacuum, washed with cold MeCN (3 mL) and Et2O (4 mL) and dried in air. X-ray crystallography revealed that the light blue needles correspond to the known complex (1) 4·2H2O.

**X-ray Crystallography:** Blue prismatic crystals of 1 (0.20 × 0.25 × 0.35 mm), 2·2H2O (0.10 × 0.25 × 0.50 mm), 2 (0.06 × 0.15 × 0.25 mm), 3·2H2O (0.30 × 0.35 × 0.50 mm) and 5·4H2O (0.20 × 0.30 × 0.30 mm) were mounted in capillaries. Diffraction measurements were made on a Crystal Logic Dual Goniometer diffractometer (for 1·2H2O, 2·2H2O and 5·4H2O) by using graphite monochromated Mo-Kα radiation and on a P2₁ Nicolet diffractometer upgraded by Crystal Logic (for 1 and 2) by using graphite monochromated Cu-Kα radiation. Unit cell dimensions were determined by using the angular settings of 25 automatically centred reflections in the range 11 < 2θ < 23° (for 1·2H2O, 3·2H2O and 5·4H2O) and 22 < 2θ < 54° (for 1 and 2). Intensity data were recorded using a 0–2θ scan. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization and psi-scan absorption corrections (for 5·4H2O) were applied by using Crystal Logic software. Important crystallographic and refinement data are listed in Table 1. The structures were solved by direct methods with SHELXS-97[22] and refined by full-matrix least-squares techniques on F² with SHELXL-97.[23] Further crystallographic details for 1: 2θ_max = 118°; reflections collected/unique/used 2562/2397: 292 parameters refined; (Δσ)_max = 0.001; (Δρ)_{max}/(Δρ)_{min} = 0.533–0.383 e/Å³; R/R_w (for all data) 0.0376/0.0989. Hydrogen atoms were located by difference maps and refined isotopically. All non-H atoms were refined anisotropically. Further crystallographic details for 2: 2θ_max = 118°; reflections collected/unique/used 3266/3062: 306 parameters refined; (Δσ)_max = 0.001; (Δρ)_{max}/(Δρ)_{min} = 0.519–0.454 e/Å³; R/R_w (for all data) 0.0486/0.1061. Hydrogen atoms were located by difference maps and refined isotopically. All non-H atoms were refined anisotropically. Further crystallographic details for 2: 2θ_max = 118°; reflections collected/unique/used 5133/4800: (Δσ)_max = 0.0197; 578 parameters refined; (Δσ)_max = 0.003; (Δρ)_{max}/(Δρ)_{min} = 0.370–0.698 e/Å³; R/R_w (for all data) 0.0530/0.1288. Hydrogen atoms were either located by difference maps and refined isotropically or introduced at calculated positions as riding on bonded atoms. All non-H atoms were refined anisotropically. Further crystallographic details for 3·2H2O: 2θ_max = 50°; reflections collected/unique/used 8306/8306: 826 parameters refined; (Δσ)_max = 0.004; (Δρ)_{max}/(Δρ)_{min} = 0.876–0.265 e/Å³; R/R_w (for all data) 0.0405/0.0939. Hydrogen atoms were either located by difference maps and refined isotopically or introduced at calculated positions as riding on bonded atoms. All non-H atoms were refined anisotropically. Further crystallographic details for 5·4H2O: 2θ_max = 48°; reflections collected/unique/used 5461/5313: 551 parameters refined; (Δσ)_max = 0.005; (Δρ)_{max}/(Δρ)_{min} = 1.095–0.721 e/Å³; R/R_w (for all data) 0.0571/0.1259. Hydrogen atoms were either located by difference maps and refined isotropically or introduced at calculated positions as riding on bonded atoms. All non-H atoms were refined anisotropically. Plots of all structures were drawn by using the Diamond 3 program package[24] CCDC-734072 (1·2H2O), -734073 (1), -734074 (2), -734075 (3·2H2O) and -734076 (5·4H2O) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Supporting Information** (see footnote on the first page of this article): Molecular structure of the cation of 1·2H2O; selected interatomic bond lengths [Å] and angles [°], hydrogen-bonding interactions and diagnostic amide and carboxylate IR bands for complexes 1, 1·2H2O, 2, 3·2H2O and 5·4H2O.

**Acknowledgments**

S. P. Raptopoulou thanks the Research Committee of the University of Patras for support (K. Caratheodory Program No 03016).

---

**Table 1. Crystallographic data for complexes 1, 1·2H2O, 2, 3·2H2O and 5·4H2O.**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Formula</th>
<th>1·2H2O</th>
<th>2</th>
<th>3·2H2O</th>
<th>5·4H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₀</td>
<td>C₄₃H₄₂Cu₂N₁₀O₁₄</td>
<td>827.66</td>
<td>863.70</td>
<td>1741.22</td>
<td>1427.13</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/c</td>
<td>P2₁</td>
<td>P2₁</td>
<td>Pn₂₁/a</td>
<td>C2/c</td>
</tr>
<tr>
<td>a [Å]</td>
<td>8.995(5)</td>
<td>9.368(5)</td>
<td>9.07(1)</td>
<td>16.409(4)</td>
<td>31.51(3)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>19.89(1)</td>
<td>10.251(5)</td>
<td>19.39(2)</td>
<td>13.26(3)</td>
<td>10.312(4)</td>
</tr>
<tr>
<td>α [°]</td>
<td>90.00</td>
<td>63.99(2)</td>
<td>92.27(4)</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>β [°]</td>
<td>95.76(2)</td>
<td>75.83(2)</td>
<td>90.86(4)</td>
<td>90.00</td>
<td>120.94(2)</td>
</tr>
<tr>
<td>γ [°]</td>
<td>90.00</td>
<td>92.27(4)</td>
<td>93.34(3)</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>V [Å³]</td>
<td>1666.5(17)</td>
<td>870.8(8)</td>
<td>1734(3)</td>
<td>570(2)</td>
<td>6802(4)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>T [°C]</td>
<td>20</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Radiation</td>
<td>Cu-Kα</td>
<td>Mo-Kα</td>
<td>Cu-Kα</td>
<td>Mo-Kα</td>
<td>Mo-Kα</td>
</tr>
<tr>
<td>λ [Å]</td>
<td>1.5418</td>
<td>0.7107</td>
<td>1.5418</td>
<td>0.7107</td>
<td>0.7107</td>
</tr>
<tr>
<td>μ [mm⁻¹]</td>
<td>2.294</td>
<td>1.307</td>
<td>2.290</td>
<td>1.565</td>
<td>1.342</td>
</tr>
</tbody>
</table>

[a] w = 1/[σ(F₀)+aP²+bP] and P = [max(Fe₁⁺;0) + 2Fe₂⁺]² + Σ[Feo-Fei]² and wR₂ = (Σ[w(Fo-Fc)²])²/Σ[w(Fo)²]. [b] For 2239 reflections with I > 2σ(I). [c] For 2786 reflections with I > 2σ(I). [d] For 4167 reflections with I > 2σ(I). [e] For 7528 reflections with I > 2σ(I). [f] For 4565 reflections with I > 2σ(I).
Maleamate(–1)/Maleate(–2)/Copper(II)–2,2′-Bipyridine Complexes


Received: May 29, 2009
Published Online: September 1, 2009