A new Cu(II) [12]metallocrown-4 pentanuclear complex based on a Cu(II)-malonomonohydroxamic acid unit†

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The first example of a Cu(II) [12]-MC-4 hydroxamic metallacrown compound containing a carboxyl group as a supporting donor function is described. The solution equilibria of malonomonohydroxamic acid (MACZ, H_2L) with Cu(II) are investigated in aqueous solution using a combination of potentiometry, UV-vis absorption spectrophotometry, EPR spectroscopy and ESI mass spectrometry. Among the four complexes fitting the best speciation model ([CuL], $[Cu_5L_4H_{-4}]^{2-}$, $[CuL_2]^{2-}$ and $[CuL_2H_{-1}]^{3-}$), a pentameric metallacrown molecule of composition Cu : L = 5 : 4 predominates in solution over the pH 4 to 11 range, and the corresponding complex was isolated in the solid state. The crystallization of the complex $[Cu_5L_4H_{-4}]^{2-}$ in the presence of $[Cu(en)_2(H_2O)_2]^{2+}$ cations resulted in the isolation of $[Cu(en)_2(H_2O)_2]_n[Cu(en)_2(H_2O)(\mu\text{-}H_2O)\{Cu_5(L_4H_{-4})(H_2O)_3\}_2]_n \cdot 20nH_2O$ (**1**), whose crystal structure has been determined by X-ray analysis. The structure of **1** consists of centrosymmetric complex cations $[Cu(en)_2(H_2O)_2]^{2+}$, infinite complex anionic chains $[Cu(en)_2(H_2O)(\mu\text{-}H_2O)\{Cu_5(L_4H_{-4})(H_2O)_3\}_2]_n^{2n-}$ and solvate water molecules. Within the complex anionic chains, the decanuclear double-decked bis([12]-MC-4) complex anions $\{Cu_5(L_4H_{-4})(H_2O)_3\}_2^{4-}$ are united by the $[Cu(en)_2(H_2O)_2]^{2+}$ complex cations due to the bridging function of the axial water molecule O(5). The magnetic behaviour of **1**, studied in the temperature range 1.8–300 K, suggests the presence of both antiferromagnetic and ferromagnetic contributions to the observed magnetic susceptibility, resulting in a ground state of $S = 2$ per formula unit.

Introduction

Metallamacrocycles are cyclic structures with metal–heteroatom units within the macrocyclic backbone substituting of carbon atoms.[1,2] Replacement of two methylene groups by –M–N– units in organic crown ethers results in inorganic metallacrown structures. A series of metallacrown complexes were obtained using aminohydroxamic acids, providing two pairs of donors, $\{O,O^-\}$–$\{NH_2,N^-\}$, able to act as the bridging unit between two metal ions. The most common are [12]metallacrown-4 complexes ([12]-MC-4), formed by β-amino- and β-hydroxy-hydroxamic acids.[1–3] There are also [15]-MC-5 structures that are able to encapsulate larger cations than Cu(II), like lanthanides[4] and even the uranyl ion.[5] In the known structures of [12]-MC-4, the sets of coordinating donors $\{O,O^-\}$–$\{NH_2,N^-\}$ or $\{O,O^-\}$–$\{NH_2,O^-\}$ do not have additional vacant donor atoms and thus are not able to bind extra metal ions to enhance the nuclearity of the formed coordination arrays. In this work, we succeeded in modifying the known metallacrown donor sets by the introduction of a carboxyl group in the β-position with respect to the hydroxamic function, leading to a $\{O,O^-\}$–$\{COO^-,N^-\}$ coordination environment around the metal ions. This distinctly changed the structural features and stability of the pentameric species when compared to the amino acid derivatives. Moreover, such a simple modification results in the formation of a [12]-metallacrown-4 compound, having vacant oxygen donor atoms in the monodentate-coordinated carboxylic groups. Taking into account the strong trend of carboxylates for bridging coordination, one may expect that such compounds can be used as precursors to obtain polynuclear complexes of higher nuclearity. Also, the ability of Cu(II) ions to form long axial contacts may be utilized for aggregation of the [12]-MC-4 units into dodecanuclear dimers.[2] Moreover, we considered the possibility of uniting the [12]-MC-4 units or their dimers into a polymeric chain with the help of additional bridging ligands or mononuclear complexes. The latter possibility has been successfully realized in our study, the results of which are reported herein.

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Experimental

All chemicals were commercial products of reagent grade and were used without further purification.

Syntheses and crystallization

The potassium salt of malonomonohydroxamic acid ($K[LH_{-1}] \cdot H_2O$) was obtained according to a reported method[6] as a white powder precipitate by the addition of 1 equiv. KOH (1 M aqueous solution) to a warm solution of MACZ, H_2L (1.19 g, 10 mmol) in water (40 cm^3), with a consequent reduction in volume of the obtained solution. Yield 1.49 g (95%). Anal. for $C_3H_6NO_5K$ (175.18) calc.: C, 20.57; H, 3.45; N, 8.00. Found: C, 20.7; H, 3.5; N, 7.8%. IR (/cm^{-1}): 1062 (ν(N–O)), 1380 ($\nu_s(COO^-)$), 1580 ($\nu_{as}(COO^-)$) and 1672 (ν(C=O) Amide I).

$[Cu(en)_2(H_2O)_2]_n[Cu(en)_2(H_2O)(\mu\text{-}H_2O)\{Cu_5(L_4H_{-4})(H_2O)_3\}_2]_n \cdot 20nH_2O$ (**1**) (where en = 1,2-diaminoethane). To a solution of $K[LH_{-1}] \cdot H_2O$ (0.175 g, 1 mmol) in water (10 cm^3) were added aqueous solutions of copper(II) nitrate (1.25 cm^3, 1 M) and potassium hydroxide (2 cm^3, 1 M) with stirring. Aqueous solutions of copper(II) nitrate (0.25 cm^3, 1 M) and ethylenediamine (0.50 cm^3, 1 M) were mixed together and then combined with the reaction itself. The obtained mixture was stirred at ambient temperature for 30 min, filtered, and the filtrate set aside for crystallization. Blue-green single crystals suitable for X-ray analysis were obtained within 48 h. Yield 0.253 g (82%). Anal. for $Cu_6C_{16}H_{54}N_8O_{31}$ (1235.92) calc.: C, 15.55; H, 4.40; N, 9.07; Cu, 30.85. Found: C, 15.3; H, 4.5; N, 8.9; Cu, 30.7%. IR (/cm^{-1}): 1045 (ν(N–O)), 1370 ($\nu_s(COO^-)$), 1580 ($\nu_{as}(COO^-)$) and 1620 (ν(C=O) Amide I).

X-Ray analysis

X-Ray data for **1** were collected on a KUMA KM-4CCD diffractometer with graphite-monochromatic Mo-K_α radiation (λ = 0.71073 Å) using the ω-2θ technique at 193(2) K. The data collection was made using Oxford Diffraction programs.[7,8] The structures were solved by direct methods (SHELXS-97)[9] and refined anisotropically by full matrix least-squares on all F^2 (SHELXL-97)[10] for all non-hydrogen atoms.

Two of the solvate water molecules (O10W and O11W) in **1** were refined with occupation factors of 0.5. The positions of the water hydrogen atoms in **1** were estimated with the HYDROGEN program.[11] The water hydrogen atoms were constrained to ride on their parent oxygen atoms with U_{iso} = 1.5 U_{eq} of the parent atom. The methylene hydrogen atoms and N–H hydrogen atoms of the coordinated ethylenediamine were positioned geometrically, and were also constrained to ride on their parent atoms with C–H = 0.98–0.99 Å, N–H = 0.92 Å and U_{iso} = 1.2 U_{eq} of the parent atom. The principal experimental parameters are given in Table 1.‡

Table 1 Crystal data and refinement parameters for compound **1**

Empirical formula	$C_{16}H_{54}Cu_6N_8O_{31}$
Formula weight	1235.91
Temperature/K	120(2)
Wavelength/Å	0.71073
Crystal system	Triclinic
Space group	*P*-1
a/Å	11.2883(4)
b/Å	13.0045(4)
c/Å	14.3048(6)
α/°	84.252(2)
β/°	82.162(2)
γ/°	88.661(2)
Volume/Å^3	2069.75(13)
Z	2
Density (calc.)/Mg m^{-3}	1.983
Absorption coefficient/mm^{-1}	3.137
F(000)	1256
Crystal size/mm	0.22 × 0.17 × 0.08
Theta range for data collection/°	2.17–27.00
Index ranges	$-14 \le h \le 14$, $-16 \le k \le 16$, $-18 \le l \le 18$
Reflections collected	41 194
Unique reflections	9041 (R_{int} = 0.0611)
Refinement method	Full matrix least-squares on F^2
Data/parameters	9041/578
Goodness-of-fit on F^2	1.027
Final *R* indices [$I > 2\sigma(I)$]	$R1$ = 0.0434, w$R2$ = 0.0933
R indices (all data)	$R1$ = 0.0811, w$R2$ = 0.1063
Largest differential peak and hole/e Å^{-3}	1.050 and −0.097

Spectroscopic and potentiometric measurements

IR spectra (KBr pellets) were recorded on a Perkin-Elmer 180 Spectrometer in the range 200–4000 cm^{-1}. Absorbance and diffuse-reflectance spectra were registered on Beckman DU 650 and UV 5240 spectrophotometers, respectively.

Electrospray mass spectra of the copper complexes with MACZ were obtained with a quadruple time-of-flight instrument (micrOTOF-Q, Bruker Daltonics, Bremen, Germany) equipped with an electrospray source. Solutions of the ligand (1.0×10^{-5} M) and 0.5 or 1 equivalent of Cu(II) prepared in a MeOH/H_2O mixture (50/50 v/v) were continuously introduced into the mass spectrometer source with a syringe pump at a flow rate of 5 µL min^{-1}. For electrospray ionization, the drying gas was nitrogen heated at 200 °C. Its flow was set at 5 L min^{-1} with a 43 psi nebulizer pressure. The capillary and skimmer voltages were set at 4000 and 40 V, respectively. The capillary exit was adjusted to 250 V. Scanning was performed from m/z = 50 to 2000 and no fragmentation process was observed.

The potentiometric experiments were carried out at a constant temperature of 25 °C under an argon flow, using a MOLSPIN automatic titration system with a Russel CMAW 711 microcombined electrode calibrated daily for hydrogen ion concentration using HNO_3. Titrations were performed on 0.1 M solutions in KNO_3 as a background electrolyte, and the ionic product of water for these conditions was $10^{-13.77}$ mol^2 dm^{-6}. Initial solutions of 2 cm^3 were titrated with NaOH, delivered by a 0.25 cm^3 micrometer syringe previously calibrated by weight titrations. Metal–ligand system titrations were performed on solutions of ligand concentration 1×10^{-3} M and 3×10^{-3} M, and Cu(II)-to-ligand molar ratios of 1 : 1, 1 : 2, 1 : 3 and 1 : 5. The potentiometric data (about

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‡ CCDC reference number 643467. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b701600j

140 points collected over a pH range 2.5–11.0) were refined with the SUPERQUAD[12] computer program.

The Cu(II)/MACZ absorption spectra were recorded on a Perkin-Elmer Lambda Bio 20 spectrophotometer with a temperature accessory. The measurements were performed at 25 °C, and the metal ion concentration was 3×10^{-3} M. Metal-to-ligand molar ratios varied from 1 : 3 to 1 : 5. The spectroscopic parameters were obtained at the maximum concentration of the particular species, as indicated by the potentiometric calculations.

Electron paramagnetic resonance spectra were recorded on a Bruker ESP 300E spectrometer at X-band frequency (9.4 GHz) and at 120 K. EPR spectra were performed in ethylene glycol–water (1 : 2 v/v) solution. The metal concentration was 5×10^{-3} M, and the metal-to-ligand ratios were 1 : 3 and 1 : 5.

Magnetic measurements

The magnetic susceptibility of a powdered microcrystalline sample of **1** in the temperature range 5–300 K, with magnetization at 2 K in the field range 0–5 T, were measured on a SQUID Quantum Design MPMS-XL-5 equipment. Corrections for diamagnetic susceptibilities were made with the help of Pascal's constants.

Results and discussion

Protonation and complex formation equilibria in aqueous solution

In order to evaluate the coordination properties of MACZ towards Cu(II) in solution, the protolytic properties of the ligand were first determined. Protonation behavior was studied by glass electrode potentiometry at T = 25 °C and I = 0.1 M (KNO_3). Malonomonohydroxamic acid (MACZ) possesses one carboxyl group and one hydroxamic unit, and in its fully protonated form, H_2L, can release two protons in the pH range 2 to 11. The statistical treatment of the potentiometric data[12] leads to two dissociation constants: pK_1 = 3.3(3) and pK_2 = 9.3(3), corresponding to ionization of the carboxylic and hydroxamic groups, respectively. The obtained values are very close to those reported in the literature for monocarboxylic and monohydroxamic acids.[13]

To quantify the interactions between the ligand and Cu(II), we have carried out a series of potentiometric titrations with metal-to-ligand molar ratios ranging from 1 : 1 to 1 : 5. The best speciation model obtained shows the formation of four complexes: [CuL], $[Cu_5L_4H_{-4}]^{2-}$, $[CuL_2]^{2-}$ and $[CuL_2H_{-1}]^{3-}$ (Table 2, Fig. 1). The possible presence of a binuclear complex, $[Cu_2L_2H_{-1}]^{-}$, was also tested, but the potentiometric data fitted notably better with the aforementioned model. The negative numbers of protons in the complexes mean deprotonation and participation in the metal binding of protons not dissociable during ligand titration performed over pH range 2 to 11.

To confirm the above speciation, UV-vis, EPR and ESI-MS experiments were carried out. The absorption spectra in the d–d region at pH < 3 exhibit a transition around 800 nm characteristic of the aquated Cu(II) ion. Around pH 4, the color of the solution becomes greenish and new bands appear: a d–d band with a maximum at 650 nm ($\varepsilon \sim 408$ $M^{-1}cm^{-1}$) and a broad charge-transfer band at 323 nm ($\varepsilon \sim 5.1 \times 10^3$ $M^{-1}cm^{-1}$). These bands persist in solution up to pH 11, moving the maximum only slightly to a lower wavelength and decreasing ε above pH 8 (Table 2). These spectral characteristics strongly support the formation of the pentanuclear $[Cu_5L_4H_{-4}]^{2-}$ complex, predominating in solution over the very wide pH range 4–11.

Table 2 Complex formation constants and spectroscopic parameters of Cu(II) complexes with MACZ in aqueous solution[a]

	Potentiometry	UV-vis		EPR	
Species	log β	λ_{max}/ nm	ε/mol^{-1} dm^3 cm^{-1}	$A_{\parallel}$/G	$g_{\parallel}$
[CuL]	8.58 (1)	796	16	140	2.36
$[Cu_5L_4H_{-4}]^{2-}$	33.93 (3)	650	408	[b]	[b]
		323	5.1×10^3		
$[CuL_2]^{2-}$	15.17 (4)	645	74	166	2.29
		323	1.0×10^3		
$[CuL_2H_{-1}]^{3-}$	5.43 (3)	645	74	166	2.29
		323	1.0×10^3		

[a] I = 0.1 M (KNO_3), T = (25.0 ± 0.2) °C. The reported errors on log β are given as 1σ and experimental errors on λ_{max} = ±2 nm. [b] EPR silent.

EPR spectra recorded on a solution at pH 3 clearly indicate the formation of a [CuL] complex, with parameters corresponding to the {O,N} mode of binding (Fig. S1,† Table 2). The complex dominating in the solution above this pH does not show an EPR spectrum, which is in agreement with the EPR behavior expected for such a type of polynuclear species (Fig. S1†).[3] The EPR spectrum reappears above pH 8, indicating the formation of mononuclear $[CuL_2]^{2-}$ and $[CuL_2H_{-1}]^{3-}$ species (Fig. S1,† Table 2). The proposed structures of [CuL], $[Cu_5L_4H_{-4}]^{2-}$, $[CuL_2]^{2-}$ and $[CuL_2H_{-1}]^{3-}$ complexes are presented in Scheme 1.

In order to obtain further evidence of the speciation model proposed above, ESI-MS experiments were carried out for the Cu–MACZ system. Although we have performed experiments

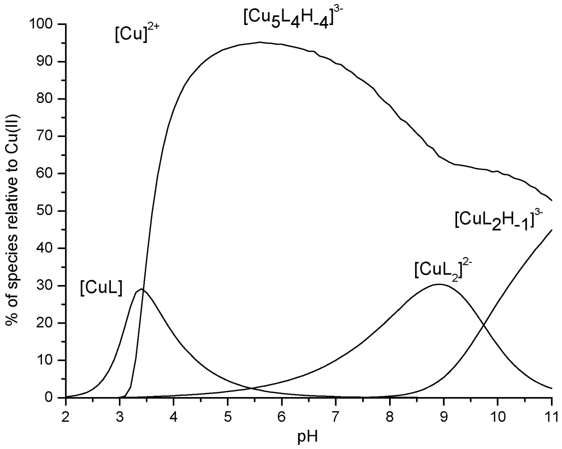
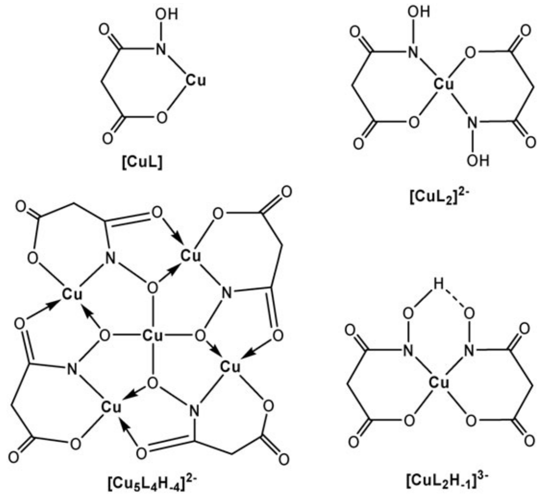


Fig. 1 Species distribution diagram for the Cu(II)–MACZ system ($c_L = 3 \times 10^{-3}$ M, $c_{Cu} = 1 \times 10^{-3}$ M, [L]/[M] = 3, where c_L = total ligand concentration and c_{Cu} = total concentration of copper).



Scheme 1 Schematic representation of the proposed structures of [CuL], $[Cu_5L_4H_{-4}]^{2-}$, $[CuL_2]^{2-}$ and $[CuL_2H_{-1}]^{3-}$ complexes.

with 1 : 1 and 1 : 2 metal-to-ligand molar ratios, we could detect only the pentameric $[Cu_5L_4H_{-4}]^{2-}$ complex (m/z_{calc} = 389.39). The ESI-MS spectra did not give any evidence of the mononuclear [CuL], $[CuL_2]^{2-}$ and $[CuL_2H_{-1}]^{3-}$ complexes, confirming that these are only minor species in solution. The experimental isotopic pattern of the negatively-charged $[Cu_5L_4H_{-4}]^{2-}$ complex was in perfect agreement with a simulated isotopic distribution.

A direct comparison of the stabilities of the pentameric species formed by the various ligands is very difficult due to the different ligand protonation pathways. Therefore, a comparison of the affinity of various ligands towards Cu(II) could be based on p*M* values at physiological pH (p*M* = –log[M(II)] under conditions of micromolar concentration of metal ion and ten-fold ligand excess). The p*Cu*(II) value of 8.5 calculated for monomalonohydroxamic acid (Table 3) is in the same range as that calculated for glutamic-γ-hydroxamic acid[14] and 2–3 orders of magnitude lower than values calculated for other aminohydroxamic acids, namely α-alaninehydroxamic acid,[15] β-alaninehydroxamic acid[3] and aspartic-β-hydroxamic acid[15] (Table 3). Lower stability of the pentameric species formed by MACZ is derived from the less effective binding ability of the carboxyl group compared to an amino group. The other consequence of this effect is seen at higher pH, when the pentameric complex may undergo decomposition to the monomeric species, clearly seen by the appearance of the characteristic EPR spectra above pH 8.

Table 3 p*Cu*(II) values for various hydroxamic acids[a]

Ligand	p*Cu*(II)	Reference
MACZ	8.50	This work
GluHA	8.53	14
α-AlaHA	11.61	15
β-AlaHA	10.38	3
β-AspHA	10.97	15

[a] p*Cu* = –log[Cu(II)] at pH = 7.4 for $c_{Cu} = 10^{-6}$ M and $c_L = 10^{-5}$ M. Abbreviations used: GluHA = glutamic-γ-hydroxamic acid, α-AlaHA = α-alaninehydroxamic acid, β-AlaHA = β-alaninehydroxamic acid, β-AspHA = aspartic-β-hydroxamic acid.

Synthesis and molecular structure of the decanuclear metallamacrocyclic complex

$[Cu(en)_2(H_2O)_2]_n[Cu(en)_2(H_2O)(\mu\text{-}H_2O)\{Cu_5(L_4H_{-4})(H_2O)_3\}_2]_n \cdot 20nH_2O$ (**1**). As shown by solution studies, MACZ, similar to other hydroxamic acids having an additional donor group in the β-position with respect to the hydroxamic function,[2] reacts with Cu(II) ions forming the pentanuclear metallacrown complex of composition Cu : L = 5 : 4. In the course of the synthesis, we used the metathesis of the counter cation ($[Cu(en)_2(H_2O)_2]^{2+}$ instead of K^+ in order to either obtain a complex of higher nuclearity or enhance the dimensionality of the polynuclear framework.

Among the reported hydroxamate 12-metallacrown-4 compounds, most are based on ligands containing an additional nitrogen-containing donor function in the β-position with respect to the hydroxamic group. The only reported crystal structures of the metallacrown with the oxygen-containing donor functions supporting the hydroxamate coordination are based on salicylohydroxamic acid,[16] *i.e.* the supporting oxygen-containing function is a phenolic group. Also, recently, a solution study of metallacrown formation with mandelohydroxamic acid (having an alcoholic OH supporting group) has been reported.[17] No ligand systems with the other oxygen-containing donor groups (in particular, carboxyl groups) capable of forming hydroxamate metallacrown compounds have been reported to date. Thus, the described complex **1** represents the first example of a hydroxamic metallacrown containing a carboxyl group as a supporting donor function.

The structure **1** is ionic and consists of centrosymmetric complex cations $[Cu(en)_2(H_2O)_2]^{2+}$, infinite complex anionic chains $[Cu(en)_2(H_2O)(\mu\text{-}H_2O)\{Cu_5(L_4H_{-4})(H_2O)_3\}_2]_n^{2n-}$ and solvating water molecules. Within the complex anionic chains, the decanuclear double-decked bis(metallacrown) complex anions $\{Cu_5(L_4H_{-4})(H_2O)_3\}_2^{4-}$ are united by $[Cu(en)_2(H_2O)_2]^{2+}$ complex cations due to the bridging function of the axial water molecule O(5). The latter unites the $[Cu(en)_2(H_2O)(\mu\text{-}H_2O)\{Cu_5(L_4H_{-4})(H_2O)_3\}_2]^{2-}$ anionic modules translating along the z-axis, thus forming polymeric columns spread along the c-direction of the crystal (Fig. 2). The neighboring anionic column $[Cu(en)_2(H_2O)_2]^{2+}$ counterions and solvate water molecules are united in the crystal by an extensive system of hydrogen bonds, where the protons derived from the water molecules or NH_2 groups of en ligands act as donors. The Cu(3) and Cu(4) atoms in both $[Cu(en)_2(H_2O)_2]^{2+}$ moieties lie on inversion centers.

Note that although, among the reported [12]-MC-4 metallacrown compounds, several complexes exhibit a dimeric decanuclear structure,[2,3,18] no compounds, in which these double-decked molecules would appear to be united into a coordination polymer have been reported up to date. In the mentioned decanuclear complexes, dimerization of the pentanuclear fragments occurs due to the long axial Cu–O contacts with the hydroxamic oxygen atoms of the neighboring fragment. The reported 1D- and 2D-polymers based on [12]-MC-4 or [15]-MC-5 metallacrown compounds involve the penta- or hexanuclear units linked into polymeric chains or 2D networks by bridging of the dimeric bis(benzoate)copper(II) building

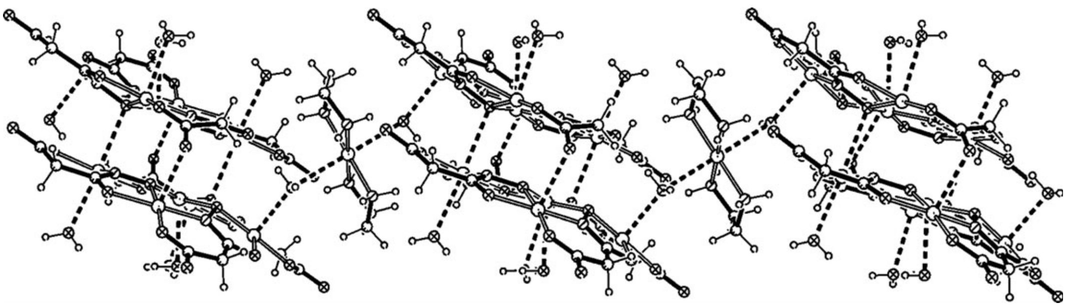


Fig. 2 Fragment of an anionic polymeric chain $[Cu(en)_2(H_2O)(\mu\text{-}H_2O)\{Cu_5(L_4H_{-4})(H_2O)_3\}_2]_n^{2n-}$ formed by the decanuclear complex anions and $[Cu(en)_2(H_2O)]^{2+}$ cations in **1**. The equatorial Cu–O and Cu–N coordination bonds are shown using unshaded lines, and the axial Cu–O contacts by dashed lines.

blocks with the bridging nitrate anions,[19] or by the adipinate or terephtalate dianions.[20]

A view of the pentanuclear metallacrown moiety of the complex anion $\{Cu_5(L_4H_{-4})(H_2O)_3\}_2^{4-}$ is shown in Fig. 3; selected bond distances and angles are given in Table 4. The decanuclear complex anion consists of two pentacopper [12]-MC-4 fragments $\{Cu_5(L_4H_{-4})(H_2O)_3\}_2^{4-}$ linked across the faces into the double-decked dimer due to binding of the hydroxamic (Cu(1C)–O(4D)($-x$, $1 - y$, $-z$) = 2.731(3) Å) and carboxylic (Cu(1B)–O(1C)($-x$, $1 - y$, $-z$) = 2.613(3) Å) oxygens of one metallacrown in axial positions to the copper atoms of a second metallacrown. Similar fused copper metallacrown structures with β-alaninehydroxamic acid and 3-hydroxyiminobutanehydroxamic acid have been already observed for a Cu(II) metallacrown by us[3] and another group.[21] The four Cu–O bonds between the metallacrowns result in a relatively stable dimer.

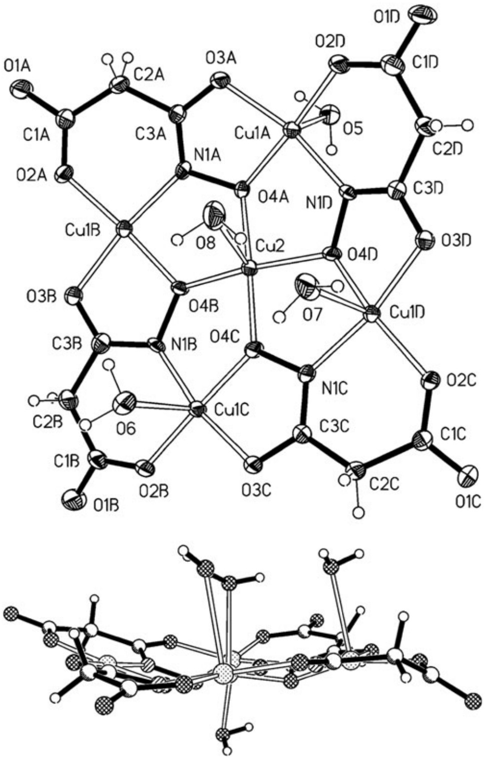


Fig. 3 Top: Structure of the pentanuclear metallacrown fragment in the complex anion in $[Cu(en)_2(H_2O)_2]_n[Cu(en)_2(H_2O)(\mu\text{-}H_2O)\{Cu_5(L_4H_{-4})(H_2O)_3\}_2]_n \cdot 20nH_2O$ (**1**) with displacement ellipsoids shown at the 40% probability level. Bottom: A side-on view.

A view of the pentacopper metallacrown fragment and the numbering scheme is presented in Fig. 3. It consists of twelve fused chelate rings (eight five-membered rings, occupying the central part of the fragment, and four six-membered rings, attached at the corners). The triply-deprotonated residues of the ligands are coordinated in double chelating and bridging modes. Each ligand forms two chelate rings and bridges the copper ion occupying the centre of the cavity, thus being bonded to three copper ions. The four peripheral copper ions are united by four diatomic hydroxamate (N,O)-bridges. Moreover, the N–O hydroxamic oxygen atoms exhibit a μ_2- or even μ_3-bridging mode, being coordinated to the central Cu(2) ion or, in the case of the O(4D) atom, to the Cu(1C) atom of the neighboring pentanuclear module within the decanuclear dimer. Thus, in the latter case, the hydroxamic O(4D) oxygen atom exhibits both in-plane and out-of-plane bridging.

Four out of the five copper atoms within the metallacrown moiety exhibit a distorted square-pyramidal geometry and one, Cu(1C), exhibits a distorted octahedral geometry with elongated axial contacts. The basal plane of the copper ion Cu(2), occupying the centre of the 12-membered metallacrown cavity, is formed by four oxygen atoms of the hydroxamic groups exhibiting a bridging function (Cu–O = 1.881(3)–1.916(3) Å), while the four copper ions involved in the metallacrown core have a mixed donor set in their equatorial coordination, formed by one nitrogen atom of the deprotonated hydroxamic group (Cu–N = 1.939(3)–1.953(3) Å) and three oxygen atoms belonging to the carboxyl and hydroxamic groups. Note that the Cu–O distances with the amide hydroxamic oxygens (1.949(3)–1.982(3) Å) are noticeably shorter than those with the N–O hydroxamic and carboxyl oxygen atoms (1.892(3)–1.935(3) Å). The apical positions are occupied either by water molecules (Cu–O = 2.401(3)–2.585(3) Å), or by the out-of-plane bridging μ_3-hydroxamic O(4D) or μ_2-carboxyl O(1C) oxygen atoms of the neighboring metallacrown module within the decanuclear dimer (Cu(1C)–O(4D)($-x$, $-y + 1$, $-z$) = 2.731(3), Cu(1B)–O(1C)($-x$, $-y + 1$, $-z$) = 2.613(3) Å). The Cu···Cu separations within the pentanuclear metallacrown module between the central (Cu(2)) and peripheral Cu atoms are in the range 3.2100(7)–3.3366(7) Å, and between the

Table 4 Selected bond lengths (Å) and angles (°) in the structure of **1**

Cu(1A)–O(2D)	1.924(3)	Cu(1C)–O(4C)	1.898(3)	Cu(2)–O(4C)	1.882(3)
Cu(1A)–O(4A)	1.935(3)	Cu(1C)–O(2B)	1.909(3)	Cu(2)–O(4D)	1.902(3)
Cu(1A)–N(1D)	1.954(3)	Cu(1C)–N(1B)	1.939(3)	Cu(2)–O(4B)	1.905(3)
Cu(1A)–O(3A)	1.982(3)	Cu(1C)–O(3C)	1.975(3)	Cu(2)–O(4A)	1.916(3)
Cu(1A)–O(5)	2.396(3)	Cu(1C)–O(6)	2.585(3)	Cu(2)–O(8)	2.554(3)
		Cu(1C)–O(4D)^a	2.731(3)	Cu(2)Cu(1C)^a	3.7316(7)
Cu(1B)–O(4B)	1.892(3)	Cu(1D)–O(4D)	1.933(3)	Cu(3)–N(4)	2.012(5)
Cu(1B)–O(2A)	1.893(3)	Cu(1D)–O(2C)	1.942(3)	Cu(3)–N(5)	2.030(5)
Cu(1B)–N(1A)	1.942(3)	Cu(1D)–N(1C)	1.944(3)	Cu(3)–O(5)	2.546(3)
Cu(1B)–O(3B)	1.955(3)	Cu(1D)–O(3D)	1.950(3)		
Cu(1B)–O(1C)^a	2.613(3)	Cu(1D)–O(7)	2.539(3)		
(2D)–Cu(1A)–O(4A)	176.4(1)	O(4C)–Cu(1C)–O(2B)	177.1(1)	O(4C)–Cu(2)–O(4D)	91.4(1)
O(2D)–Cu(1A)–N(1D)	91.4(1)	O(4C)–Cu(1C)–N(1B)	87.9(1)	O(4C)–Cu(2)–O(4B)	88.0(1)
O(4A)–Cu(1A)–N(1D)	91.6(1)	O(2B)–Cu(1C)–N(1B)	93.1(1)	O(4D)–Cu(2)–O(4B)	164.7(1)
O(2D)–Cu(1A)–O(3A)	96.0(1)	O(4C)–Cu(1C)–O(3C)	81.2(1)	O(4C)–Cu(2)–O(4A)	176.2(1)
O(4A)–Cu(1A)–O(3A)	80.7(1)	O(2B)–Cu(1C)–O(3C)	97.7(1)	O(4D)–Cu(2)–O(4A)	91.5(1)
N(1D)–Cu(1A)–O(3A)	163.6(1)	N(1B)–Cu(1C)–O(3C)	169.0(1)	O(4B)–Cu(2)–O(4A)	88.5(1)
O(2D)–Cu(1A)–O(5)	95.2(1)	O(4C)–Cu(1C)–O(6)	95.2(1)	O(4C)–Cu(2)–O(8)	99.7(1)
O(4A)–Cu(1A)–O(5)	86.0(1)	O(2B)–Cu(1C)–O(6)	87.5(1)	O(4D)–Cu(2)–O(8)	88.5(1)
N(1D)–Cu(1A)–O(5)	101.9(1)	O(4C)–Cu(1C)–O(4D)^a	87.3(1)	O(4B)–Cu(2)–O(8)	106.7(1)
O(3A)–Cu(1A)–O(5)	92.0(1)	O(2B)–Cu(1C)–O(4D)^a	90.0(1)	O(4A)–Cu(2)–O(8)	82.9(1)
O(4B)–Cu(1B)–O(2A)	174.2(1)	O(6)–Cu(1C)–O(4D)^a	177.3(1)		
O(4B)–Cu(1B)–N(1A)	89.4(1)	O(4D)–Cu(1D)–O(2C)	161.8(1)	N(4)^b–Cu(3)–N(4)	180.0(2)
O(2A)–Cu(1B)–N(1A)	94.1(1)	O(4D)–Cu(1D)–N(1C)	90.6(1)	N(4)–Cu(3)–N(5)	84.9(2)
O(4B)–Cu(1B)–O(3B)	81.5(1)	O(2C)–Cu(1D)–N(1C)	92.2(1)	N(4)–Cu(3)–N(5)^b	95.1(2)
O(2A)–Cu(1B)–O(3B)	94.7(1)	O(4D)–Cu(1D)–O(3D)	81.1(1)	N(5)–Cu(3)–N(5)^b	180.000(1)
N(1A)–Cu(1B)–O(3B)	170.0(1)	O(2C)–Cu(1D)–O(3D)	98.1(1)	N(4)^b–Cu(3)–O(5)	85.6(1)
O(4B)–Cu(1B)–O(1C)^a	93.7(1)	N(1C)–Cu(1D)–O(3D)	168.8(1)	N(4)–Cu(3)–O(5)	94.4(1)
N(1A)–Cu(1B)–O(1C)^a	89.7(1)	O(4D)–Cu(1D)–O(7)	96.35(11)	N(5)–Cu(3)–O(5)	94.9(2)
		N(1C)–Cu(1D)–O(7)	87.61(12)	N(5)^b–Cu(3)–O(5)	85.1(2)

Symmetry transformations used to generate equivalent atoms:^{a} $-x, -y + 1, -z$. ^{b} $-x, -y + 1, -z - 1$.

metallacrown core Cu atoms are in the range 4.5634(7)–4.6204(7) Å. In general, the observed geometrical parameters are close to those reported for previously studied hydroxamic metallacrowns.[2,16,21]

The hydroxamic ligands are triply-deprotonated (by the carboxyl, and by both N–H and O–H functions of the hydroxamic groups). The N–O fragments of the hydroxamic group are in a *cis* position with respect to the carboxyl groups, which is conditioned by participation of both the hydroxamic nitrogen and carboxyl oxygen atoms in the formation of the six-membered chelate rings. The C–O, N–O and C–N distances are normal for deprotonated, coordinated carboxyl and hydroxamic groups.

The $[Cu(en)_2(H_2O)_2]^{2+}$ cations in the structure (both involved in bridging with the decanuclear complex anion and acting as counterions) are centrosymmetric, with the central atoms occupying special positions so that the coordination polyhedra are of D_{4h} point symmetry, and the copper and donor nitrogen atoms lie in the same plane. The complex cations consist of two ethylenediamine molecules, which chelate the central atoms in the equatorial plane, and two axially-coordinated water molecules. The geometrical parameters of both described complex cations are very close to those reported for the other centrosymmetric $[Cu(en)_2(H_2O)_2]^{2+}$ cations.[22,23] The axial Cu–O contacts in both polyhedra (2.546(3) and 2.574(3) Å) are significantly longer than the equatorial Cu–N bond lengths (1.998(4)–2.030(6) Å) due to the Jahn–Teller effect. The bite angles are reduced to 84.9(2) and 85.1(2)°. The five-membered chelate rings in both cations indicate a *gauche* conformation, with the carbon atoms deviating from the CuNN planes by 0.17(1)–0.42(1) Å.

The $[Cu(en)_2(H_2O)_2]^{2+}$ cation, playing a bridging function between the translational decanuclear complex anion, exhibits a slightly shorter Cu–O distance (2.546(3) Å) than the counterion (2.574(3) Å). Interestingly, the water molecules bridging the en-containing complex cation and bis(metallacrown) complex anion indicate significantly shorter Cu–O contacts with the anionic copper atom (Cu(1A)–O(5) = 2.396(3) Å) than with the $Cu(en)_2^{2+}$ (Cu(3)–O(5) = 2.546(3) Å). The angle Cu(1A)–O(5)–Cu(3) is 148.2(1)° and the Cu(1A)···Cu(3) separation is 4.7630(6) Å. The EPR spectrum of **1** gives a very broad pseudo-symmetric signal.

Magnetic properties

Complex **1** was subjected to magnetic susceptibility measurements in the temperature range 1.8–300 K and magnetization measurements at 2 K in the magnetic field range 0–5 T. Plots of the product $\chi_M T$ *vs.* T and $M/N\beta$ *vs.* H are presented in Fig. 4a and b, respectively (where M = molar magnetization, N = Avogadro number and β = Bohr magneton). The molar susceptibilities were corrected for diamagnetism with the help of Pascal's constants,[24] and also for temperature independent paramagnetism, estimated at 60×10^{-6} cm^3 K mol^{-1} per Cu(II) ion. The room temperature value of the $\chi_M T$ product (1.72 cm^{-3} K mol^{-1} per twelve copper ions) for **1** is much smaller than the expected value for twelve uncoupled spins (21.01 cm^{-3} K mol^{-1}), and is indicative of strong

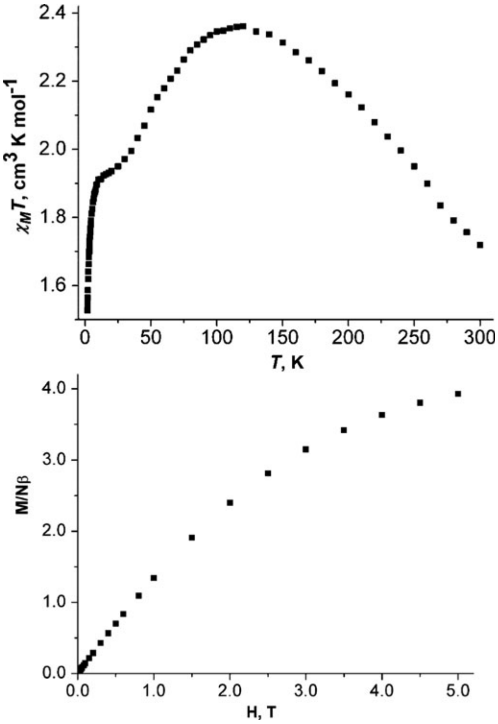


Fig. 4 Temperature dependence of the product $\chi_M T$ (top) and the field dependence of the magnetization at 2 K (bottom) for **1** (per twelve Cu atoms).

antiferromagnetic coupling within the coordination array. The temperature dependence curve of the $\chi_M T$ product exhibits quite an unusual shape; on cooling, $\chi_M T$ first grows slowly, reaching a maximum at 120 K (2.36 cm^{-3} K mol^{-1}), then it starts to drop more rapidly down to the room temperature value (1.72 cm^{-3} K mol^{-1}) at 3.3 K. On further cooling, the product $\chi_M T$ starts to diminish very steeply, reaching a value of 1.53 cm^{-3} K mol^{-1} at 1.8 K. Magnetization measurements (Fig. 4b) revealed that the $M/N\beta$ value at high magnetic fields approaches a value close to 4, which is clearly indicative of the ground state with four uncoupled spins.

Taking into account the 1D-polymeric structure of the complex, featuring alternating mono- and decanuclear units, it seems quite difficult to ascribe the observed effects to specific superexchange pathways and to calculate the corresponding exchange parameters. The only report in the literature detailing a study of the magnetic properties of a pentanuclear Cu(II) hydroxamate [12]MC-4 complex[21] revealed the presence of strong antiferromagnetic interactions, both between the terminal ions and between the terminal and the central Cu ions, thus giving rise to a spin doublet. At the first approximation, we assumed that in **1**, a similar exchange interaction scheme may be realized within the pentanuclear units, and attempted to examine the cryomagnetic behavior of **1** by trying to fit the $\chi_M T$ temperature dependence with a model, envisaging the presence of four isolated spin doublets arising from two non-interacting $[Cu(en)_2(H_2O)_2]^{2+}$ cations obeying the Curie–Weiss law and two non-interacting pentanuclear arrays with a global antiferromagnetic interaction mediated by two magnetic couplings, *J*1 and *J*2 (between the terminal Cu ions and between the central and the terminal Cu ions, respectively), with a common *g* value. We found the fitting to be impossible as the curvature of the obtained function significantly differs from that of the observed $\chi_M T$ *vs*. *T* dependence in the whole range of reasonable values of *J*1, *J*2 and *g*. In particular, a significant increase in the $\chi_M T$ product over the temperature range 300–120 K cannot be described by this model, and thus can be indicative of the presence of additional weak ferromagnetic interactions (mediating the inter-dimeric exchange interaction (*J*3) within the decanuclear array, and maybe also mediating the interaction between the $[Cu(en)_2(H_2O)_2]^{2+}$ cations and the decanuclear complex anions along the polymeric chain (*J*4)) that cannot be neglected. However, for such cases with three or four different *J* values, it is not possible to derive analytical expressions from the spin Hamiltonian.

In particular, a model envisaging a ferromagnetic interaction between the two pentanuclear metallacrown units looks quite reasonable. The room temperature $\chi_M T$ value (1.72 cm^{-3} K mol^{-1} per twelve copper ions) is somewhat below that expected for two magnetically isolated spin doublets plus a spin triplet (1.75 cm^{-3} K mol^{-1} for $g = 2$). The saturation magnetization value also corroborates this model. The expected temperature behaviour would be an increase of the $\chi_M T$ product on cooling, reaching a plateau close to *ca*. 1.90 K mol^{-1}, which corresponds to the completely populated spin triplet with $g \approx 2.1$. However, the $\chi_M T$ product temperature dependence reaches a quasi plateau with a maximum $\chi_M T$ value equal to 2.36 cm^{-3} K mol^{-1}, which is much greater than that envisaged by the regarded model. In our opinion, this effect can be conditioned by the presence of an additional weak ferromagnetic interaction between the ferromagnetically-coupled decanuclear modules and the $[Cu(en)_2(H_2O)_2]^{2+}$ cations along the polymeric chain through axial Cu–O contacts (in fact, the observed $\chi_M T$ value at 120 K is close to that calculated for one spin quartet plus a spin doublet, 2.25 cm^{-3} K mol^{-1} for $g = 2$). The observed decrease of the $\chi_M T$ value on cooling below 120 K is mainly due to zero field splitting of the triplet state and also probably due to the inter-chain antiferromagnetic interactions.

Magnetic studies of **1** demonstrate that in spite of the fact that the Cu(II) hydroxamate [12]MC-4 complexes exhibit global antiferromagnetic coupling, the pentanuclear complex anions may be used as building blocks for the assembly of discrete exchange clusters of high nuclearity and coordination polymers showing ferromagnetic behavior.

Conclusion

Solution and X-ray studies on the Cu(II) complexes of malonohydroxamic acid (MACZ) have demonstrated the first example of a Cu(II) [12]-MC-4 hydroxamic metallacrown compound produced by the hydroxamic ligand, having an additional carboxyl donor function disposed in the β-position with respect to the hydroxamic group. Although less stable, when compared to aminohydroxamic derivatives, the pentanuclear complex predominates in aqueous solution over a large pH range. In pentanuclear molecule **1**, the carboxyl groups are coordinated in a monodentate fashion to copper ions, which makes room for the incorporation of the second carboxyl oxygen atom into a metal–oxygen bond with an extra metal ion, with the realization of different bridging modes for the carboxylate. This opens up the possibility of obtaining metal complexes of higher nuclearity (in particular, mixed metal assemblies) by the use of pentanuclear metallacrown complex anions as ligands in reactions with metal salts, or cationic complexes with labile monodentate ligands in the coordination sphere. Structure **1** described above represents an example of such a possibility; a self-dimerization leading to the formation of dodecanuclear anionic aggregates and their consequent linking into a 1-D polymeric chain. This example clearly demonstrates that the well known trend of hydroxamic acids forming stable pentanuclear metallacrown compounds can be utilized for the preparation of high nuclearity complexes, where the metallacrown compounds themselves can be used as building blocks in reactions with metal complexes. Analysis of the molecular topology of the earlier reported hydroxamate metallacrown complexes[1–5,17,18] revealed that they do not have many favourably arranged vacant donor atoms for growing high nuclearity complexes. The elaboration of synthetic routes to high nuclearity assemblies derived from malonomonohydroxamate metallacrowns is currently under way in our laboratories.

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