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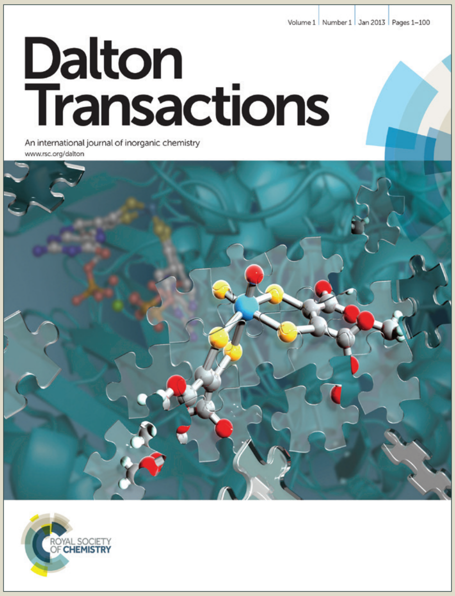

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Communication

A unique 1-amino-1-cyclopropane carboxylate cupric-cryptate hosting sodium

Wadih Ghattas,[a] Rémy Ricoux,[a] Hafsa Korri-Youssoufi,[a] Régis Guillot,[a] Eric Rivière[a] and Jean-Pierre Mahy*[a]

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The first cluster containing acc was prepared *via* supramolecular self-assembly. This Cu(II) cluster traps Na$^+$ as shown in the solid state by the crystal structure and in solution by ESI-MS. Further characterisations revealed a ferromagnetic intracluster exchange and an irreversible reduction with a rapid intracluster electron transfer.

The developments in the field of supramolecular coordination chemistry have enabled the synthesis of complicated molecular structures in a designed and predetermined manner using multidentate ligands.[1] A notable example is the progress in the design of Cu(II)–amino acid complexes from simple mononuclear complexes to one– and finally poly–dimensional cluster chains.[2] Initially, the interest in these clusters arose due to their role as models for metal-protein interactions.[2a] More recently they have been perceived as inorganic analogues of cryptands (metallacryptate) because they trap exogenous metal ions. The importance of such metallacryptates derive from their intrinsic exciting physical properties (magnetic, electrochemical, photophysical), which are in contrast difficult to obtain with organic cryptands.[2b-h] Herein, we report the synthesis and characterisation of a Cu(II)–cluster comprising 1-amino-1-cyclopropane carboxylate (acc) in its backbone and trapping a sodium cation in a central cage. 1-amino-1-cyclopropane carboxylic acid (accH) is a non-proteogenic natural amino acid abundant in plants, where it is oxidised by the metallo-oxidoreductase acc–oxidase (ACCO) to produce the phytohormone ethylene.[3] Structurally characterised acc/H containing metal complexes are rare, with few examples reported in the studies of the mechanism of ACCO, none of which is a metal cluster.[4]

Blue crystalline complex $[Na\subset Cu_2\{Cu(acc)_2\}_4(ClO_4)_5(H_2O)_2] \cdot 2H_2O$ (**1**) was quantitatively obtained following a method described by Wang *et al.* for the synthesis of $[Na\subset Cu_2\{Cu(proline)_2\}_4(ClO_4)_5CH_3OH] \cdot H_2O$ but starting from accH instead of L–proline.[2c] The resolved X-ray crystal structure (Fig. 1) reveals six Cu(II) forming a metal framework in a pseudo octahedral geometry in which a trapped Na$^+$ is the inversion center. Four Cu(II) form the base of the framework octahedron (4 Cu$_{equ}$), each of which has six coordinates and is in an elongated octahedral geometry. The eight axial positions of the four Cu$_{equ}$ are on the plane of the base of the framework and are occupied by four bridging perchlorate molecules, which link two Cu$_{equ}$ each. The four equatorial positions of each Cu$_{equ}$ are perpendicular to the base of the framework and are occupied by two acc molecules, each of which is bound to the Cu$_{equ}$ by the nitrogen of the amino group and by one oxygen from the carboxylate group. The same oxygen atoms from all carboxylate groups bind the Na$^+$ in the center of the cluster via electrovalent bonds. Two Cu(II) form the cap of the framework octahedron (2 Cu$_{axial}$) and have five coordinates each in a square pyramidal geometry with an elongated axial position external to the centre of the framework and occupied by a water molecule. The four ligands, which form each of both squared bases, are the other oxygen atoms of the carboxylate functions. Each structurally asymmetric unit is formed by the forth of **1** yielding a P$\bar{1}$ space group with each unit cell formed by the packing of four asymmetric units on four opposing sides.

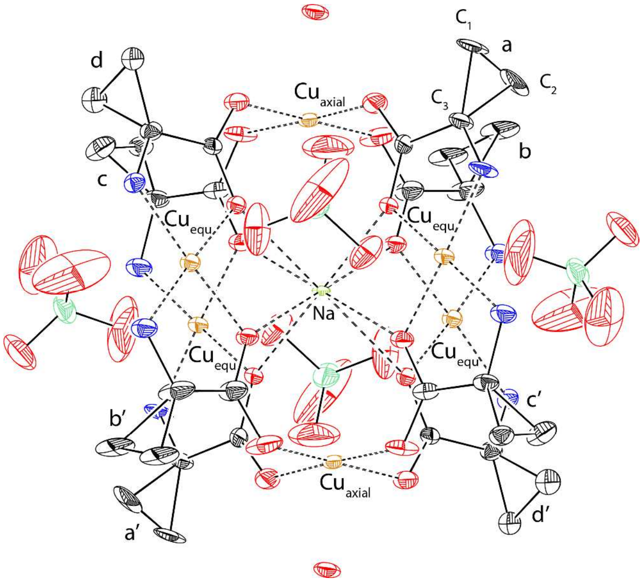


Fig. 1 ORTEP drawing of the crystal structure of $[Na\subset Cu_2\{Cu(acc)_2\}_4(ClO_4)_4(H_2O)_2]^+$ cation (ADP at 40% probability level). Equatorial coordination bonds and the electrovalent Na$^+$—O$_{acc}$ bonds are displayed in dotted lines. Axial coordination bonds (Cu—O$_{H2O}$ and Cu—O$_{ClO4}$) and all hydrogen atoms are omitted for more clarity.

The Cu—O$_{H2O}$ bond length and the average Cu—O$_{ClO4}$ bond length (2.23 Å and 2.58 Å, respectively) reflect the loose binding of these elongated axial ligands. The average Na$^+$—O$_{acc}$, Cu$_{axial}$—

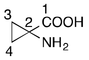
O_{acc} and Cu_{equ}—O_{acc}, Cu_{equ}—NH_2 distance are 2.578 Å, 1.927 Å, 1.934 Å and 1.980 Å, respectively, and are all similar to those observed in resembling six–Cu(II)–amino acid clusters (Table 1).[2b-g]

Table 1: Average lengths for selected bonds observed in resembling six-copper-amino acid complexes.

Six-copper-amino acid complexes	Average bond length (Å)				Space group
	Na—O	Cu_{axial}—O	Cu_{equ}—O	Cu_{equ}—N	
Glycine[2e]	2.603	1.947	1.952	1.995	$P\bar{1}$
Alanine[2b, 2f]	2.587	1.931	1.930	1.966	P1, C_2
acc[this work]	2.578	1.927	1.934	1.980	$P\bar{1}$
Threonine[2d]	2.576	1.959	1.948	1.972	$P2_1$
Proline[2b, 2c]	2.549	1.960	1.934	1.998	I4, I4
4-hydroxy-proline[2c]	2.562	1.951	1.943	2.005	$P2_1$

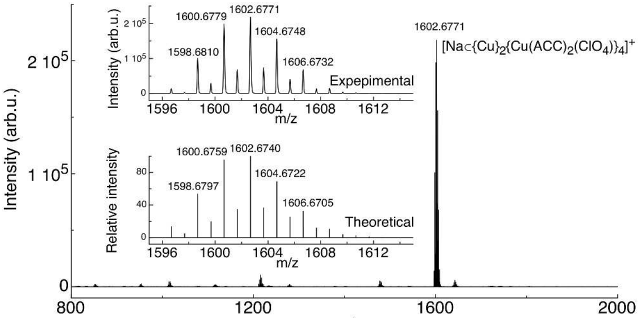
Similar C_3—C_4 bond lengths (1.47-1.55 Å) and C_3—C_2—C_4 angles (58.2-60.5 º) are observed for each of the four pairs of acc molecules (Fig. 1: a a', b b', c c' and d d'). These bond lengths and angles are also within the usual range reported for acc/accH containing metal complexes (Table 2).[4]

Table 2: Selected bond lengths and angles from all acc/H containing crystal structures of metal complexes.

Bond length (Å) C_3—C_4	Angle (º) C_3—C_2—C_4	References 
1.470(18)	58.2(8)	Fig. 1, fragment a
1.509(17)	60.5(7)	Fig. 1, fragment b
1.55(4)	60(3)	Fig. 1, fragment c
1.514(19)*	60.5(10)*	Fig. 1, fragment d
1.508(19)*	60.2(10)*	
1.480(17)	59.2(7)	$Cu(acc)_2$[4b]
1.483(6)	59.2(2)	$[Cu(1,10\text{-phenanthroline})(acc)]ClO_4$[4c-d]
1.482(5)	59.2(3)	$[Cu(2,2'\text{-bipyridine})(acc)]ClO_4 . H_2O$[4a]
1.469(9)	58.9(4)	$[Cu(2\text{-picolylamine})(acc)]ClO_4$[4c-d]
1.427(12) 1.493(10)	57.6(5) 59.7(4)	$[Fe_2(1,4,7\text{-triazacyclononane})_2(\mu\text{-}O)(\mu\text{-}accH)_2]ClO_4 . H_2O$[4e]

Average values are reported for structures with more than one acc/H per unit cell. *For fragment d two values are given because of a disorder over two sets of sites with a 0.5/0.5 occupancy ratio.

Fig. 2 (+)-ESI mass spectrum of **1**. Top insert: zoom around m/z 1602.



Bottom insert: theoretical isotopic distribution for $[Na\subset Cu_2\{Cu(acc)_2\}_4(ClO_4)_4]^+$.

ESI mass spectrometry experiments were carried out following recently reported conditions to detected similar Cu(II)–amino acid cluster by mass spectrometry.[2g] Results reveal an intense pseudomolecular ion matching both theoretical mass and isotopic distribution of $[Na\subset Cu_2\{Cu(acc)_2\}_4(ClO_4)_4(H_2O)_2^+ - 2(2H + O)]^+$ (Fig. 2). The loss of four hydrogen atoms and two oxygen atoms can be assigned to the loss of the two water molecules of the cation of **1**. Accordingly in the crystal structure these water molecules appear loosely bound. Conversely, the similarly loosely coordinated perchorate anions appear to withstand the ESI mass conditions.

Temperature dependence of the magnetic susceptibility χ_m is reported in the form of $\chi_m T$ vs. T per cluster unit (Fig. 3, left) and reveals overall a typical ferromagnetic material behavior.[2d-g] Collected data were corrected from the contribution of the sample holder and from diamagnetic contributions deduced using Pascal's constant tables. Nevertheless, at 300 K the corrected $\chi_m T$ value is 1.4 emu.mol^{-1}.K compared to an expected 2.25 emu.mol^{-1}.K (six S = ½ centres with g = 2). This difference may result from an additional diamagnetic contribution from the compound (χ_m^{dia}). Based on the crystal structure the magnetic orbitals (d_{x2-y2}) of the Cu_{axial} centres are perpendicular to those of the Cu_{equ}, therefore a ferromagnetic exchange (J_1') is expected. The magnetic orbitals of the all-adjacent Cu_{equ} are also perpendicular but distant because of the elongated Cu—ClO_4^- bonds, hence a week ferromagnetic exchange (J_2') is expected. In order to calculate the intracluster coupling constants two possible models (**A** and **B**) were compared at fitting χ_m T vs. T. In **A** both J_1' and J_2' were taken into account whereas in **B** J_2' was considered negligible. In both models χ_m^{dia} and the function χ_m^{para} were obtained by solving the Heisenberg Spin-Hamiltonian (H) corresponding to each model using MAGPACK package to which a minimisation routine was added.[5]

For **A**:

$$\mathrm{H} = -2\mathrm{J}_1'\left(\vec{\mathrm{S}}_{1_{\mathrm{axial}}} + \vec{\mathrm{S}}_{2_{\mathrm{axial}}}\right)\left(\vec{\mathrm{S}}_{3_{\mathrm{equ}}} + \vec{\mathrm{S}}_{4_{\mathrm{equ}}} + \vec{\mathrm{S}}_{5_{\mathrm{equ}}} + \vec{\mathrm{S}}_{6_{\mathrm{equ}}}\right) - 2\mathrm{J}_2'\left(\vec{\mathrm{S}}_{3_{\mathrm{equ}}} + \vec{\mathrm{S}}_{5_{\mathrm{equ}}}\right)\left(\vec{\mathrm{S}}_{4_{\mathrm{equ}}} + \vec{\mathrm{S}}_{6_{\mathrm{equ}}}\right)$$

For **B**:

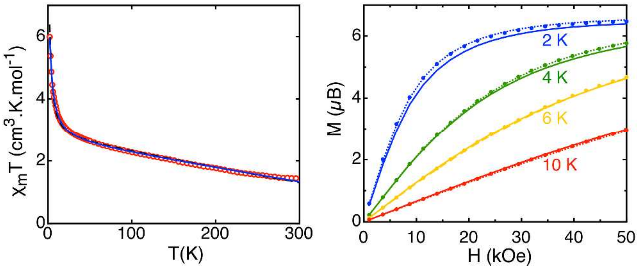
$$H = -2J_1'\left(\vec{S}_{1_{axial}} + \vec{S}_{2_{axial}}\right)\left(\vec{S}_{3_{equ}} + \vec{S}_{4_{equ}} + \vec{S}_{5_{equ}} + \vec{S}_{6_{equ}}\right)$$

Where $\vec{\mathrm{S}}_{\mathrm{i\,=\,1\,to\,6}}$ is the spin operator of each of the six Cu(II) ($\vec{\mathrm{S}}_{\mathrm{i}} = 1/2$).

The errors in the fits were calculated from the following expression in which fit and obs stand for the fitted and the experimentally observed data, respectively.

$$R = \left[\sum (fit - obs)^2 / \sum obs^2\right]$$

Fig. 3 Left: Experimental $\chi_m T$ vs. T (red circles), fit according to **A**



(dashed black lines) and fit according to **B** (solid bleu line). Right: Experimental M *vs.* H (dots), fit according **A** (solid lines) and fit according **B** (dashed lines).

The best fits to experimental $\chi_m T$ vs. T obtained for **A** resulted from: $J_1' = 2.60$ cm^{-1}, $J_2' = -9.27\ 10^{-1}$ cm^{-1}, g = 2.16, $\chi_{diam} = -4.42\ 10^{-3}$ cm^3.mol^{-1} and for **B** from $J_1' = 1.53$ cm^{-1}, g = 2.19, $\chi_{diam} = -4.78\ 10^{-3}$ cm^3.mol^{-1}. Both models fit the experimental data well with $R\chi_m T = 1.35\ 10^{-4}$ and $7.48\ 10^{-4}$, respectively (Fig. 3, left). Nevertheless, **A** gave an antiferromagnetic J_2' contrary an expected ferromagnetic exchange. Additionally, isothermal measurements of the magnetisation (M) were performed and both sets of parameters were used to fit the experimental M *vs.* H (Fig. 3, right). Only the parameters obtained form **B** gave a good fit with $RM = 0.44\ 10^{-4}$ while those of **A** gave $RM = 0.48\ 10^{-3}$, therefore only model **B** is consistent with the experimental data. Finally, the saturation value of the magnetisation is 6.4, which is close to the value of 6.5 expected for an S = 3 state with g = 2.19.

All six–Cu(II)–amino acid clusters of similar geometry present the magnetic behaviour described herein i.e. a week ferromagnetic intracluster coupling with comparable values for J_1', a negligible J_2' and a ground spin state of 3 (Table 3).

Table 3: Magnetic exchange constants of resembling six–Cu(II)–amino acid clusters.

J_1' (cm^{-1})	Cluster
1.79	*catena*-[Na⊂Cu_2{Cu(glycine)$_2$}$_4$(ClO_4)$_5$$H_2O$] · H_2O[2e]
0.64	[Na⊂Cu_2{Cu(alanine)$_2$}$_4$(ClO_4)$_5$$H_2O$] · 4$H_2O$[2f]
1.72	[Na⊂Cu_2{Cu(proline)$_2$}$_4$(ClO_4)$_5$$CH_3OH$] · H_2O[2c]
1.39	*catena*-Na⊂Cu_2{Cu(4-hydroxyl-proline)$_2$}$_4$(ClO_4)$_5$[2c]
0.43	[Na⊂Cu_2{Cu(threonine)$_2$}$_4$(ClO_4)$_5$(H_2O)$_2$] · 5H_2O[2d]
1.53	[Na⊂Cu_2{Cu(acc)$_2$}$_4$(ClO_4)$_5$(H_2O)$_2$] · 2H_2O

J_1' is the magnetic exchange between axial and equatorial Cu(II) centers. For all these clusters the magnetic exchange between neighbouring Cu(II) centers (J_2') was either considered or found to be negligible after fittings.

Electrochemical characterisations of Cu(II)-amino acid clusters surprisingly have not been reported despite the interest in the physical properties of such metallacryptants. We initiated the study using cyclic voltammetry (CV) and square wave voltammetry (SWV). CV curves obtained at different scan rates (Fig. 4, left) show a single, diffusion dependent (Fig. 4, left, insert) reduction wave that can be assigned to the irreversible reduction of clustered Cu^{2+} to Cu^{+}. The reduction potential Cu^{2+}/Cu^{+} at 200 mV.s^{-1} is $E_{red} = 0.60$ mV which is comparable to that of naturally occurring Cu(II)–amino acid clusters.[6] On the one hand, the irreversibility is rationalised by the differences in geometry and coordination between Cu(II) and Cu(I). Hence the reduction of the Cu(II) cluster into Cu(I) leads to an unstable species which rearranges. On the other hand, a single reduction wave observed for six Cu(II) centres is justified by the assembly of cluster **1.** This assembly of two different kinds of copper centres (Cu_{equ} and Cu_{axial}) linked by the same carboxylate ligands that trap a central Na^{+} could be responsible for a rapid intracluster electron transfer and therefore a single reduction wave. Nevertheless, SWV reveal two broad reduction peaks (0.012 mV and 0.364 mV, Fig. 4, right) that can be assigned to the reduction of the first and the second kind of Cu(II) centres. However the peak to peak ratio is not 2:1 as expected from 4 Cu_{equ}:2 Cu_{axial}. Consequently, there is no complete electronic isolation between the copper centres at the time scale of the SWV experiment.

In summary, we prepared and characterised the first acc-containing metal cluster. This cluster is a metallacryptate that traps Na^{+}. At low temperature, an intracluster ferromagnetic exchange was detected. Finally, CV and SWV characterisations revealed an irreversible reduction and a rapid intracluster electron transfer.

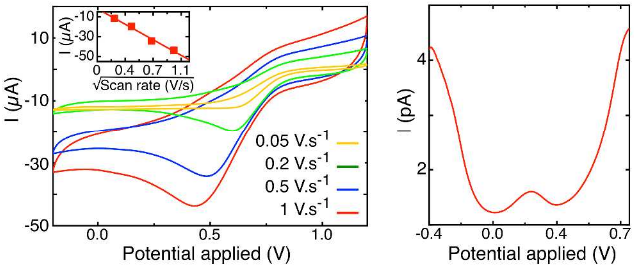


Fig. 4 Left: CV curves at different scan rates. Insert: Peak currents *vs.* square root of scan rates. Right: SW voltammogram.

Notes and references

[a] *Institut de Chimie Moléculaire et des Matériaux d'Orsay (UMR CNRS 8182), Université Paris Sud, Orsay, 91405 CEDEX, France. Fax: 0033169157421; Tel: 0033169157421; E-mail: jean-pierre.mahy@u-psud.fr.*

† Electronic Supplementary Information (ESI) available: Detailed synthesis, elemental analysis and UV-Vis spectrophotometric characterisation. Additional magnetism and electrochemistry experimental data. Further X-ray crystallograpic information and CIF format file. See DOI: 10.1039/b000000x/

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Graphical abstract

Exploiting the self-assembly of $Cu(ClO_4)_2$, amino acids and Na^+ we prepared and full caracterised the first 1-amino-1-cyclopropane containing metal cluster.

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