An Na_8 Cluster in the Structure of a Novel Oxamato-Bridged Na^ICu^{II} Three-Dimensional Coordination Polymer

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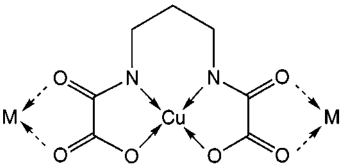
The new heterometallic sodium(I)-copper(II) compound Na_4Cu_2 (**2**) · 10.5 H_2O (**3**), where H_8[**2**] stands for *N*,*N*′,*N*′′,*N*′′′-methanetetrayltetrakismethylenetetrakis(oxamic acid), has been synthesized and its crystal structure determined by single-crystal X-ray diffraction. The structure of **3** consists of cationic $[Cu_2(\eta^4:\eta^4\text{-}\mathbf{2})]^{4-}$ dinuclear units, coordinated sodium cations, and water molecules. In the crystal, the dinuclear copper entities are joined through discrete aggregates of eight sodium atoms linked by oxamato and water bridges, leading to a three-dimensional polymeric network.

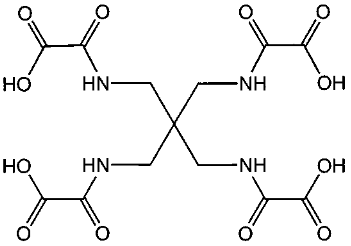
The chemistry of polymetallic coordination compounds (clusters or cages) has received much attention during the last two decades because of their fundamental role in redox metalloenzymes[1] and metal storage proteins.[2] The recent finding that polymetallic complexes could exhibit intrinsically original magnetic properties, such as high-spin molecules (nanomagnets), has further enhanced the interest in cluster chemistry.[3] Metal clusters with different kinds of bridging ligands (both organic and inorganic) are known for almost all transition metals throughout the periodic table,[4] including among them the class of polyoxometalates.[5] The preparation of these clusters has been frequently based on the use of organic terminal ligands to prevent the formation of undesired polymeric solids. Otherwise, the use of metal complexes as ligands in the preparation of cluster compounds is an attractive approach to obtain heterometal aggregates. This can be realized using suitable precursor complexes with exposed donor atoms which ligate another metal site.

We have always been interested in the coordination chemistry of oxamato ligands like H_4[**1**], the parent acid of the polychelating ligand *N*,*N*′-propane-1,3-diylbis(oxamate). The fully deprotonated ligand forms a stable copper(II) complex $[Cu(\eta^4\text{-}\mathbf{1})]^{2-}$, where the tetradentate ligand coordinates to Cu^{II} through the two strongly basic amide-N and the two carboxylate-O atoms,[6] while the four carbonyl-O atoms are still sufficiently basic to coordinate to another metal ion in a bischelate fashion (Scheme 1). That provides diverse examples of heterometallic compounds with both first-row transition[7] and rare-earth lanthanide metal ions.[8] In particular, this family of compounds ranges from discrete mononuclear[6] or small oligonuclear complexes[7b,7c] (dimers and trimers) to extensive infinite chain arrays[7a,8c] and layers,[8a,8b] although no three-dimensional networks are reported.



Scheme 1. Coordination modes of the *N*,*N*′-propane-1,3-diylbis(oxamato) ligand: tetradentate-*N*,*N*,*O*,*O* (full arrows) and bis(bidentate-*O*,*O*) (dashed arrows)

In the scope of our continuous research in this field we prepared the related binucleating ligand H_8[**2**], the parent acid of the ligand *N*,*N*′,*N*′′,*N*′′′-methanetetrayltetrakismethylenetetrakis(oxamate). Potentially, this ligand can bind two Cu^{II} ions to give a dimeric copper(II) complex $[Cu_2(\eta^4:\eta^4\text{-}\mathbf{2})]^{4-}$, which in turn can act as ligand, as its monomeric counterpart. We report herein the synthesis and general physical and structural characterization of the sodium salt of this oxamatocopper(II) complex of formula $Na_4[Cu_2(\eta^4:\eta^4\text{-}\mathbf{2})]$ · 10.5 H_2O (**3**).



H_8[**2**]

The structure of **3** comprises dimeric copper(II) complex anions $[Cu_2(\eta^4:\eta^4\text{-}\mathbf{2})]^{4-}$, complexed sodium metal cations and solvent water molecules, both coordinated and noncoordinated (Figure 1). Within the dinuclear copper anion,

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the Cu(1) and Cu(2) atoms are coordinated to the two deprotonated amide-N and two carboxylate-O atoms of the bistetradentate ligand in a nearly square-planar geometry [metal deviations from the mean basal planes are 0.020(4) and 0.188(5) Å, respectively], with Cu(2) showing a weak axial interaction with the oxygen atom O(16) from water (2.80 Å). The average Cu−N and Cu−O bond lengths (1.92 and 1.97 Å, respectively) and the copper bond angles (84.0−96.6°) are similar to those found for the related monomeric complex $(PPh_4)_2[Cu(\eta^4\text{-}\mathbf{1})] \cdot 2\ H_2O$.[6] The conformation of the ligand is such that the two mean copper basal planes form a dihedral angle of 44.0°, thus a global butterfly-folded shape to the dinuclear copper molecule.

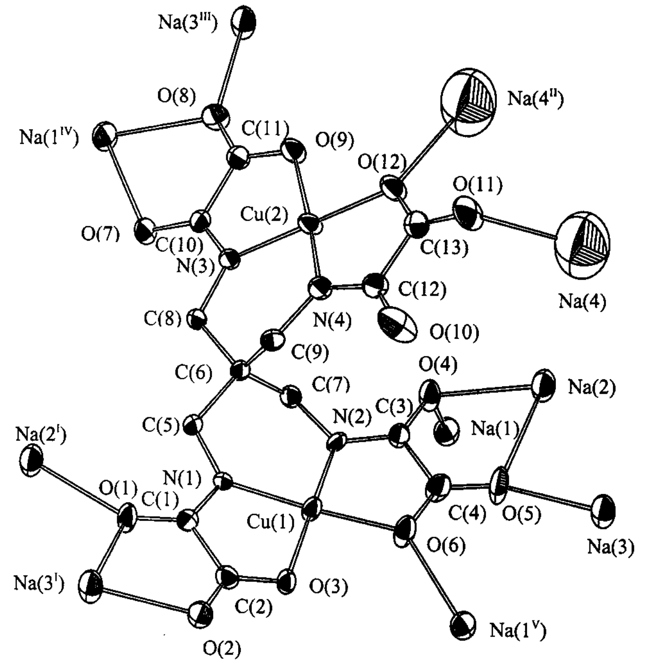

Figure 1. Perspective drawing of the assymetric unit of **3** with the atom-numbering scheme; thermal ellipsoids are representted at the 30% probability level (all hydrogen atoms and oxygen atoms from water molecules have been omitted for clarity); selected bond lengths [Å] and angles [°] with standard deviations in parentheses: Cu(1)−N(1) 1.926(5), Cu(1)−N(2) 1.919(5), Cu(1)−O(3) 1.961(4), Cu(1)−O(6) 1.964(4), Cu(2)−N(3) 1.929(5), Cu(2)−N(4) 1.921(5), Cu(2)−O(9) 1.963(4), Cu(2)−O(12) 1.983(4); N(2)−Cu(1)−N(1) 96.6(2), O(3)−Cu(1)−N(1) 84.5(2), O(6)−Cu(1)−N(1) 173.3(2), N(2)−Cu(1)−O(3) 176.8(2), N(2)−Cu(1)−O(6) 84.2(2), O(6)−Cu(1)−O(3) 95.1(2), N(3)−Cu(2)−N(4) 95.1(2), O(9)−Cu(2)−N(3) 84.4(2), O(12)−Cu(2)−N(3) 178.9(2), N(4)−Cu(2)−O(9) 172.4(2), N(4)−Cu(2)−O(12) 84.0(2), O(12)−Cu(2)−O(9) 96.4(2)

The dinuclear copper anion molecule is dissymmetric both (*R*) and (*S*) optical isomers are present in the crystal due to the existence of an inversion center according to the *P*−1 space group]. In fact, the central carbon atom C(7) connecting the two mononuclear copper fragments turns out to be the center of dissymmetry of the molecule because of the four independent oxamato substituents are involved in distinct coordinative interactions with the metal sodium cations (i.e., the central C atom in the free ligand $H_8[\mathbf{2}]$ can be seen as being "prochiral"). Actually, almost all twelve oxygen atoms [but O(10)] from the four oxamato groups of the dicopper complex anion participate in coordination of the sodium metal cations. These sodium cations form in turn molecular aggregates comprising of eight Na^+ which are connected through the $[Cu_2(\eta^4{:}\eta^4\text{-}\mathbf{2})]^{4-}$ moieties, thus leading to an intricate three-dimensional structure in the solid-state (Figure 2). The Cu(1)···Cu(2) intramolecular separation is 5.92 Å, while the shortest intermolecular ones $Cu(1^V)\cdots Cu(1^{VI})$ and $Cu(2^{II})\cdots Cu(2^{VI})$ are 5.28 and 4.08 Å, respectively (II = 1 − *x*, 2 − *y*, 2 − *z*; V = −*x*, 1 − *y*, 1 − *z*; VI = *x*, 1 + *y*, *z*).

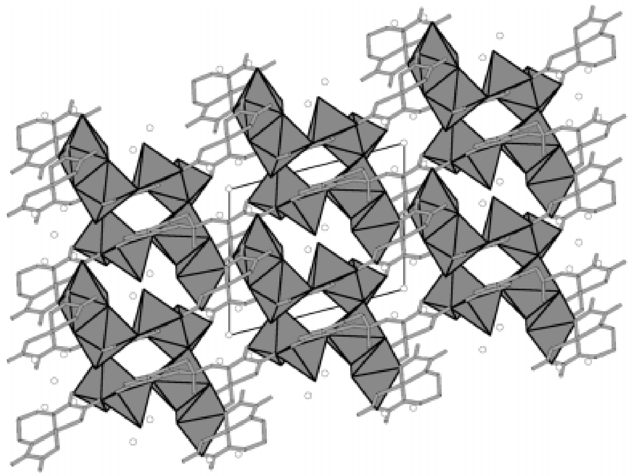

Figure 2. Projection view of the unit cell of **3** along the *b* axis, showing the formation of octanuclear sodium aggregates in the solid state; sodium cations are represented by shaded octahedra and all remaining atoms are represented by spheres of arbitrary radii

The octanuclear sodium cationic entity (Figure 3) is made up of two tetranuclear propeller-like molecular units with an approximate three-fold symmetry related by an inversion center (V = −*x*, 1 − *y*, 1 − *z*). The central tris(chelate) sodium complex of one tetrameric fragment and its symmetry related one have opposite chirality, one isomer being Δ and the other Λ (i.e., the centrosymmetric octanuclear moiety is mesomorphic). Alternatively, the resulting cluster can also be viewed as a ring of six sodium atoms with two edge-bridged sodium atoms. Therefore, all but two pairs of neighboring sodium polyhedra in the aggregate share an edge, while Na(1) and $Na(3^V)$ atoms (and their symmetry-related pair) share a corner. The central hexasodium ring is reminiscent to that found in some cyclic hexairon(III)[9a] and hexamanganese(III) complexes.[9b] The six sodium atoms which form the ring are situated at the vertices of an almost regular hexagon [Na(1)−Na(2), Na(2)−Na(3) and $Na(3)-Na(1^V)$ distances of 3.52, 3.44 and 3.70 Å, respectively, and $Na(2)-Na(1)-Na(3^V)$, Na(3)−Na(2)−Na(1) and $Na(2)-Na(3)-Na(1^V)$ angles of 118.9, 116.9 and 105.4°, respectively], with a diameter of about 6.92 Å (average distance between two opposing symmetry-related sodium atoms). The remaining Na(4) and $Na(4^V)$ atoms are connected to the ring through Na(2) and $Na(2^V)$ atoms, respectively [Na(2)−Na(4) distance of 3.50 Å]. The intraring sodium atoms lie essentially in a plane with a maximum deviation of ±0.467(2) Å for Na(2) and $Na(2^V)$, whereas the extraring ones are ±2.58(1) Å out of the ring plane.

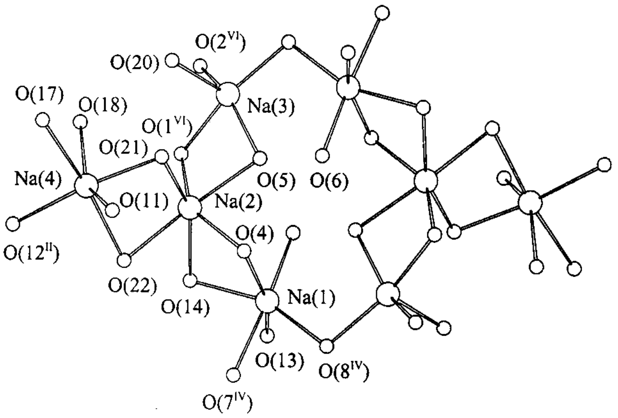

Figure 3. Perspective drawing of the cationic octasodium cluster of **3** with the atom-numbering scheme; an inversion center relates one tetranuclear unit to the other one; atoms are represented by spheres of arbitrary radii; selected bond lengths [Å] and angles [°] with standard deviations in parentheses: Na(1)−O(4) 2.513(6), $Na(1^{V})$−O(6) 2.368(5), Na(1)−$O(7^{IV})$ 2.384(5), Na(1)−$O(8^{IV})$ 2.379(5), Na(1)−O(13) 2.421(7), Na(1)−O(14) 2.395(6), Na(2)−$O(1^{VI})$ 2.299(5), Na(2)−O(4) 2.358(5), Na(2)−O(5) 2.485(5), Na(2)−O(14) 2.463(6), Na(2)−O(21) 2.366(10), Na(2)−O(22) 2.539(9), Na(3)−$O(1^{VI})$ 2.357(5), Na(3)−$O(2^{VI})$ 2.386(5), Na(3)−O(5) 2.346(5), $Na(3^{V})$−$O(8^{IV})$ 2.291(5), Na(3)−O(20) 2.345(10), Na(4)−O(11) 2.532(10), Na(4)−$O(12^{II})$ 2.615(9), Na(4)−O(17) 2.532(10), Na(4)−O(18) 2.540(14), Na(4)−O(21) 2.302(14), Na(4)−O(22) 2.52(2); Na(2)−O(4)−Na(1) 92.3(2), Na(1)−O(14)−Na(2) 92.7(2), Na(2)−$O(1^{VI})$−Na(3) 95.4(2), Na(3)−O(5)−Na(2) 90.8(2), Na(4)−O(21)−Na(2) 97.0(5), Na(4)−O(22)−Na(2) 87.4(4), $Na(3^{V})$−$O(8^{IV})$−Na(1) 104.7(2) [symmetry codes: (II) $1 - x, 2 - y, 2 - z$; (IV) $-x, 1 - y, 2 - z$; (V) $-x, 1 - y, 1 - z$; (VI) $x, 1 + y, z$]

Focusing on the core skeleton of the cationic Na_8 cluster, the six sodium atoms which define the central ring are linked by ten bridging oxygen atoms: four carboxylate-O and four carbonyl amide-O atoms from the oxamato groups and only two water molecules. Bis(aquo) bridges connect the two extraring sodium atoms to the central Na_6 skeleton. The remaining sites of the six $[NaO_6]$ octahedra and two $[NaO_5]$ trigonal bipyramids which form the octasodium aggregate are occupied by oxygen atoms from additional water molecules and oxamato ligands. The Na−O bond lengths are not all equivalent (2.29−2.66 Å), and the O−Na−O angles lie in the large range 69.6−166.7°. The architecture of the sodium cluster is issued from the bridging modes of the oxamato groups: each of the two μ_4-O_3C_2NR moieties link four Na^+ ions in the inner rim of the cyclic ring, while each of the four μ_2-O_2C_2ONR moieties link two Na^+ ions in the outer rim. In addition, two bidentate bridging carboxylate moieties from two μ_2-O_2C_2ONR groups connect the extraring Na^+ ions from two neighboring aggregates.

In summary, compound **3** provides a clear evidence of self-assembly in the solid-state of an unprecedent octanuclear sodium cluster which serves as the molecular fragment of a three-dimensional supramolecular complex. In that case, the formation of the octasodium cluster relies on the multidentate character of the novel dicopper oxamato complex $[Cu_2(\eta^4{:}\eta^4\text{-}\mathbf{2})]^{4-}$, acting as both terminal and bridging ligand. We are currently focusing our attention on the ability of this novel organometallic assembling block to bind more relevant cations in the field of magnetochemistry, such as iron and manganese, in order to elaborate new materials with interesting magnetic properties (molecular-based magnets)

Experimental Section

Preparation of H_8[2]: The tetraethyl ester Et_4H_4[**2**] ligand resulted from the condensation of tetrakis(aminomethyl)methane prepared according to a literature procedure[10] and diethyl oxalate in tetrahydrofuran: A solution of the tetraamine (4.0 g, 30 mmol) in THF (100 mL) was added dropwise through a dropping funnel to a large excess of diethyl oxalate (250 mL). The resulting mixture was stirred for 0.5 h at room temp. and then filtered through paper. The solvent was removed in a rotatory evaporator and the remaining oil was treated with diethyl ether to give a white solid which was collected by filtration and dried under vacuum (90%). − ^1H NMR ($[D_6]$DMSO): $\delta = 1.29$ (t, 12 H, CH_3), 3.02 (d, 8 H, CH_2N), 4.27 (q, 8 H, CH_2O), 8.89 (t, 4 H, NH). − IR (KBr): $\tilde{\nu} = 3330\ cm^{-1}$ (NH), 1740 and 1695 (C=O).

Synthesis of 3: The sodium salt of the copper(II) complex **3** was obtained by reaction of the tetraethyl ester Et_4H_4[**2**] with Cu^{2+} in basic aqueous media: To a suspension of Et_4H_4[**2**] (1.33 g, 2.5 mmol) in water (50 mL) was added an aqueous solution (25 mL) of NaOH (1.00 g, 25 mmol). After stirring for 15 min at room temp. until complete dissolution, an aqueous solution (25 mL) of $Cu(NO_3)_2 \cdot 3\ H_2O$ (1.20 g, 5 mmol) was added dropwise. The deep-blue solution was then filtered to eliminate the rest of solid particles and the solvent volume was reduced to 25 mL in a rotatory evaporator when a solid began to appear. Slow addition of absolute ethanol to the mother liquor gave a purple-blue crystalline solid which was collected by filtration and air-dried. Upon standing a second crop separated which was also collected and dried (95%). − IR (KBr): $\tilde{\nu} = 1640$ and $1608\ cm^{-1}$ (C=O). − $C_{13}H_8Cu_2N_4Na_4O_{12} \cdot 8\ H_2O$ (775): calcd. C 20.14, H 3.12, N, 7.23; found C 19.35, H 2.85, N 7.01. − The purple-blue crystalline solid is readily soluble in water but insoluble in common solvents (even in DMSO or DMF). Well-shaped large purple prisms of **3**, suitable for X-ray diffraction, were obtained by recrystallization from concentrated aqueous solutions after two weeks of slow concentration at room temp.

X-ray Crystallographic Study for 3:[11] Crystal data: $C_{13}H_{29}Cu_2Na_4N_4O_{22.5}$, mol. mass = 820, triclinic, space group $P{-}1$, $a = 10.507(1)$, $b = 10.958(2)$, $c = 13.438(2)$ Å, $\alpha = 109.17(1)$, $\beta = 99.21(1)$, $\gamma = 103.11(1)°$, $V = 1376.3(3)$ Å^3, $d = 1.99\ g\ mL^{-1}$, $Z = 2$. − Data collection: Enraf-Nonius CAD-4 diffractometer, Mo-K_α radiation, $\lambda = 0.71069$ Å, graphite monochromator, 293 K, ω-2θ, Lorentz and polarization effects and absorption correction, $\mu = 1.72\ mm^{-1}$, $2.0° \le \theta \le 22.5°$, crystal size $0.05 \times 0.20 \times 0.05$ mm. 3498 unique reflections, and 3428 assumed as observed with $I > 2\sigma(I)$. Structural analysis and refinement: standard Patterson methods with subsequent full-matrix least-squares method refinement, SHELX93.[12] The hydrogen atoms from the organic ligand were located from a difference synthesis and refined with an overall isotropic thermal parameter. The hydrogen atoms from the water molecules were neither found nor calculated. Refinement of 414 variables with anisotropic thermal parameters for all non-hydrogen atoms gave $R = 0.051$ and $R_w = 0.123$ with $S = 1.05$. The crystal drawings were carried out with the SCHAKAL[13] and CRYSTAL MAKER[14] programs.

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[11] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101560. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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