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Formation of polynuclear architectures with copper atoms and 1,1-cyclohexanediacetate anions

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The reaction of copper nitrate $Cu(NO_3)_2 \cdot 3H_2O$ with potassium salt of 1,1-cyclohexanediacetic acid (H_2CHDAA) in an EtOH—toluene mixture affords the polymeric complex $\{[(EtOH)_2Cu_2(CHDAA)_2] \cdot EtOH\}_n$ (**1**). The addition of pyridine to the $Cu(NO_3)_2 \cdot 3H_2O$—K_2CHDAA reaction system in an EtOH—MeCN mixture results in the isolation of the unusual octadecanuclear heterometallic cluster $[K_2(\eta^1\text{-}H_2O)_6(\eta^1\text{-py})_8Cu_{16}(\eta^1\text{-OH})_2(\mu_4\text{-CHDAA})_{16}] \cdot EtOH \cdot MeCN \cdot 3H_2O$ (**2**). In complex **2**, the hexadecanuclear metal carboxylate dianion $(\eta^1\text{-}H_2O)_6(\eta^1\text{-py})_8Cu_{16}(\eta^1\text{-OH})_2(\mu_4\text{-CHDAA})_{16}$ acts as the metal-containing macropolycyclic ligand. The newly synthesized compounds **1** and **2** were characterized by X-ray diffraction and EPR.

Key words: synthesis, polynuclear copper complexes, 1,1-cyclohexanediacetate anions, X-ray diffraction study, EPR.

Dicarboxylic acids act as polydentate bridging ligands and often play the structuring role in the formation of coordination polymers.[1—3] However, in some cases it is impossible to reliably determine the structures of these compounds and, as a consequence, to interpret with certainty their properties because of their poor solubility. For example, according to the published data, only four adequately characterized complexes with 1,1-cyclohexanediacetate anions and transition metal atoms have been isolated, two of which have an island structure,[4,5] whereas two other complexes are polymers.[6]

At the same time, the geometric features of these dianions and their conformational flexibility are such that these organic units can be used in the design of unusual architectures with transition metal atoms, including cyclic systems, analogous to the known "rings" with chromium and iron atoms bound to monocarboxylic acid anions.[7,8] Evidently, this can lead to the formation of more complex architectures of polycyclic metal-containing cores. Hence, these systems can be considered as promising metal-containing "crowns" suitable for the extraction of other metal ions, for example, of alkali metal ions, from solution.

In the present study, we investigated the possibility of the formation of polynuclear complexes with different geometries starting from the copper(ɪɪ) nitrate—potassium 1,1-cyclohexanediacetate (K_2CHDAA) system by the self-assembly in solution and also studied the effect of the addition of pyridine on the formation of polynuclear structures.

Results and Discussion

It appeared that the reaction of copper(ɪɪ) nitrate with potassium 1,1-cyclohexanediacetate (K_2CHDAA) taken in a ratio of 1 : 1 in ethanol (60 °C) affords the polymeric complex $\{[(EtOH)_2Cu_2(CHDAA)_2] \cdot EtOH\}_n$ (**1**). According to the X-ray diffraction data, the Cu^{II} atoms in the chain of compound **1** are arranged in pairs to form a ribbon, the dinuclear moiety $\{(EtOH)_2Cu_2(CHDAA)_2\}$ being the formal repeating unit of polymer **1** (Fig. 1). Polymer **1** is formed by the dinuclear tetracarboxylate metal fragments $\{(EtOH)_2Cu_2(CHDAA)_4\}$ linked together (Cu...Cu, 2.5786(17) Å). This is not surprising because it is well known that copper tends to form dinuclear structures with four bridging carboxylate groups.[9,10] All Cu atoms in compound **1** are equivalent and are in a distorted tetragonal-pyramidal coordination environment formed by four O atoms of the bridging carboxyl groups (Cu—O, 1.914(7)—1.988(7) Å) and one O atom of the coordinated ethanol molecule (Cu—O, 2.157(7)—2.176(7) Å). Four carboxylate groups belong to four different CHDAA^{2-} dianions. Two pairs of dicarboxylate dianions form a bridge with two adjacent dinuclear moieties of polymer **1** through the coordination of the second carboxylate group.

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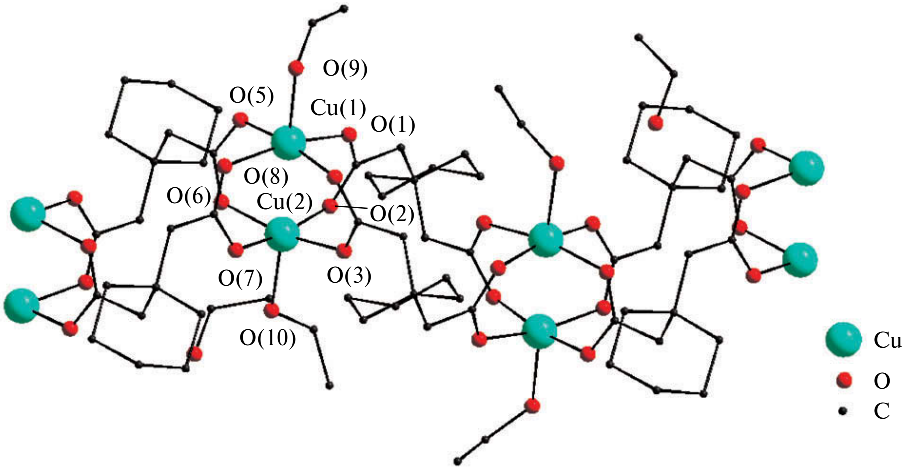

Fig. 1. Structure of the polymeric chain in $\{[(EtOH)_2Cu_2(CHDAA)_2]\cdot EtOH\}_n$ (**1**) (hydrogen atoms are not shown).*

The addition of pyridine to the reaction mixture of $Cu(NO_3)_2\cdot 3H_2O$ and K_2CHDAA in an EtOH—MeCN solution leads to the formation of the unusual heteronuclear complex $[K_2(\eta^1\text{-}H_2O)_6(\eta^1\text{-py})_8Cu_{16}(\eta^1\text{-OH})_2(\mu_4\text{-CHDAA})_{16}]\cdot EtOH\cdot MeCN\cdot 3H_2O$ (**2**). If the reagents are taken in the ratio [Cu] : [K_2CHDAA] : py = 1 : 1 : 2, the yield of compound **2** is low (5%). However, if the ratio between the metals in the starting reagents is close to the composition in the resulting cluster **2** (Cu : K = 16 : 2), the yield increases to 48.5%. In this case, the deficient acid anions are compensated by the addition of the tetrabutylammonium salt.

The copper-containing carboxylate moiety in compound **2** is formed by eight equivalent dinuclear moieties $\{Cu_2(py)(X)(\mu\text{-OOC—})_4\}$ (X = H_2O or OH; Cu...Cu, 2.6044(10)—2.6055(9) Å). As in polymer **1**, each dinuclear moiety has a structure of the dinuclear tetracarboxylate complex (Fig. 2, *a*) (Cu—O(CHDAA), 1.946(4)—1.997(4) Å; Cu—N, 2.139(4)—2.173(5) Å; Cu—O, 2.195(4)—2.199(5) Å). Each $CHDAA^{2-}$ dianion of the dinuclear moiety is linked to four analogous dinuclear fragments $\{Cu_2\}$ through the second carboxyl group. This binding results in the formation of the macropolycyclic three-dimensional system topologically similar to a square antiprism. From the geometric point of view, the complex formation is formulated as the necessity of the choice of a polyhedron with eight vertices (each vertex is the dinuclear moiety $\{Cu_2(py)(X)(\mu\text{-OOC—})_4\}$ such that four edges come into each vertex. If each axial pyridine ligand is considered as a tail, whereas a water molecule or an OH group is considered as a head, the heads of the dinuclear moieties are oriented inside the antiprism (Fig. 2, *c*). Although all axial X ligands are structurally equivalent, six ligands are formally water molecules, whereas two ligands are OH groups.

Compound **2** has a unique macropolycyclic structure. To our knowledge, neither carboxylate analogs nor compounds containing a similar metal core are available in the Cambridge Structural Database. The hexadecanuclear dication acts as a complex metal-containing bis-macrocyclic ligand with respect to potassium ions. The O atoms of the carboxylate groups bound to one K atom are involved in the crown-like macrocycle formed by four eight-atom equivalent moieties. Each moiety is formed by a Cu atom, the O atom (interacting with the K ion) of the carboxyl group coordinated to Cu, the C atom of the same carboxyl group, three C atoms, which link the carboxyl groups of one cyclohexanediacetate anion, the C atom of the second carboxyl group of the same dianion, and the O atom of the carboxyl group bound to the latter C atom (formally, 32-crown-8). Four axial O-donor ligands bound to the copper atoms of this macrocycle are, in turn, also bound to the potassium ion and form an architecture resembling complexes with calixarenes. Two potassium cations in complex **2** (K...K, 6.024 Å) are incorporated into two cavities open from the side of the square faces of the antiprisms. The coordination environment of the K atom can be described as a square antiprism formed by four O atoms of four bridging carboxyl groups (K—O, 2.791(4)—2.812(4) Å) and four O atoms of water molecules and/or OH groups (K—O, 2.883(6)—2.887(6) Å) (Fig. 2, *b*). The molecule has the crystallographic symmetry *P*4/*n*; the fourfold axis passes through the K ions occupying the cavity of the molecule (Fig. 2, *a*, *b*).

Apparently, we can speak about the template assembly of the macropolycyclic dianion on two potassium ions.

All equivalent atoms (including the copper atoms and the electron-donating atoms of the axial ligands) occupy the vertices of their own antiprisms. The copper atoms form two square antiprisms: the outer antiprism (the

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* Figures 1 and 2 are available in full color in the on-line version of the journal (http://www.springerlink.com).

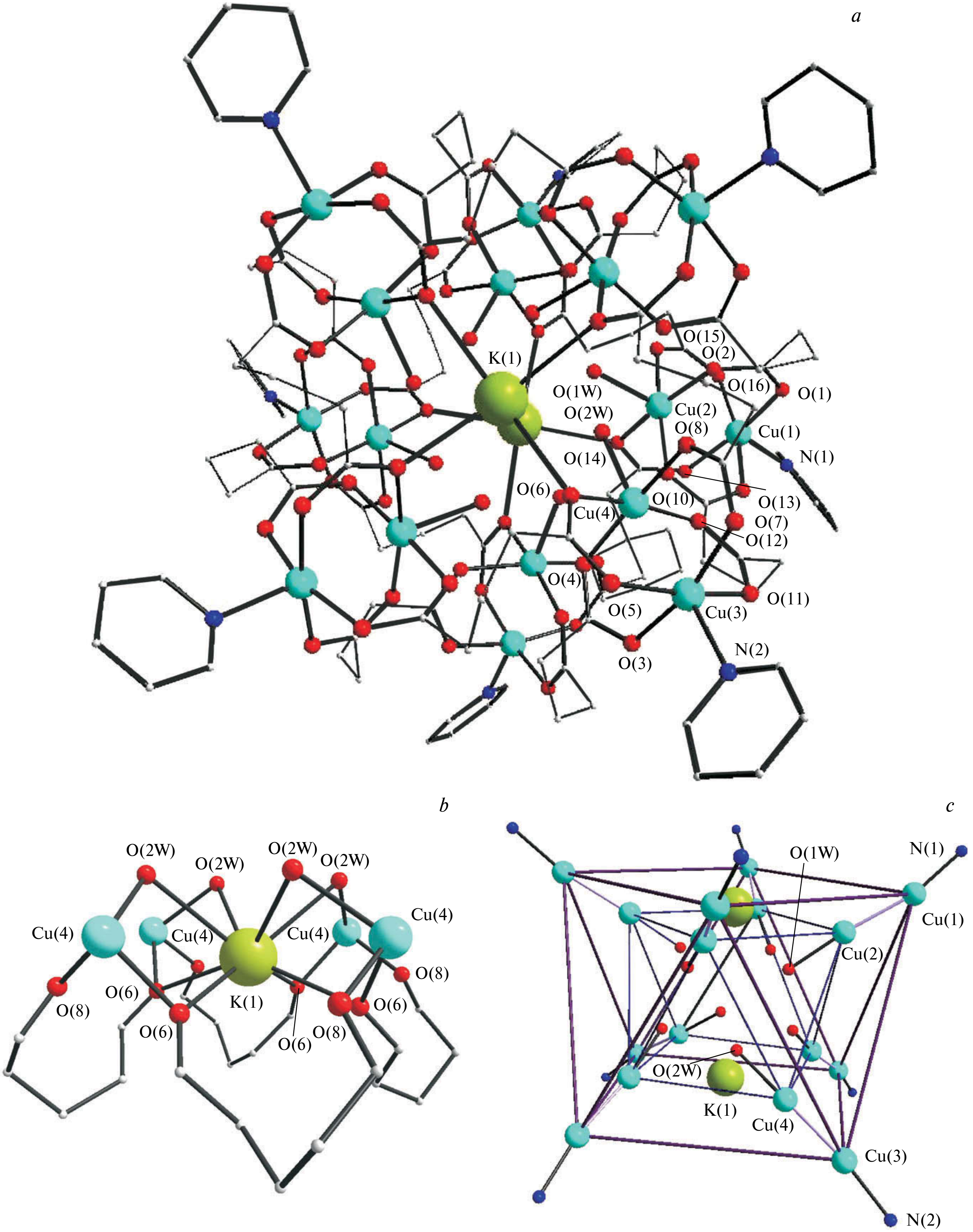

Fig. 2. Molecular structure of complex **2** (*a*) (hydrogen atoms and the cyclohexane moiety of dicarboxylic acid are not shown); the coordination environment of the potassium atom in complex **2** (*b*); the metal core of complex **2**, a system of square antiprisms of the copper atoms is shown (*c*).

Cu...Cu edge lengths are 8.223 and 8.257 Å) and the inner antiprism (the Cu...Cu edge lengths are 5.209 and 5.230 Å). The geometric sizes of the cluster molecule correspond to the sizes of the antiprism formed by the hydrogen atoms of the pyridine ligands in the *para* positions with respect to the nitrogen atoms (the H...H edge lengths are 13.60 and 13.28 Å).

The EPR spectra of complexes **1** and **2** (Figs 3 and 4) are characteristic of systems in the triplet state (copper dimers) with the total spin $S = 1$. The prerequisite for the existence of polynuclear complexes in the triplet state is a strong exchange interaction between metal ions.[11—13] The EPR spectra of these systems are characterized by the resolved structure due to the zero-field splitting, as well as by half-field transitions with $\Delta m_S = 2$. The positions of the lines in the magnetic field are determined by the values of the g tensor and the zero-field splitting tensor D. In the case when the D value (in the frequency units) is comparable with or higher than the detection frequency of the EPR spectrometer, the total spectrum not always can be experimentally recorded, as is presented in Fig. 3. This figure shows the X-band EPR spectra (the characteristic frequency is 9.5 GHz) of the known classical dinuclear copper(II) pivalate $[py_2Cu_2(piv)_4]$ and compounds **1** and **2**. The spectra of polynuclear structures **1** and **2** (Fig. 3, *b*, *c*) consist of three absorption lines in magnetic fields of ~500, 4900, and 6000 G. It should be noted that the first line was recorded only partially. The Q-band EPR spectra (the characteristic frequency is 34 GHz) showed all absorption lines, as is illustrated in Fig. 4. The absorption lines in magnetic fields of ~7100 G (H_z), 9700 G (H_{xy^1}), and 13500 G (H_{xy^2}) correspond to allowed transitions, at which the spin projection changes by $\Delta m_S = 1$. Another characteristic feature of the *Q*-band EPR spectrum is that the absorption lines are observed in the magnetic field of ~5000 G ($H_{1/2}$). This half-field line corresponds to the forbidden transition ($\Delta m_S = 2$) and is indicative of the dinuclear structure of the compound. The position of the line in the magnetic field of about 11000 G (H_{dq}) corresponds to that expected for this forbidden transition ($\Delta m_S = 2$) with absorption of two microwave quanta, although the high intensity of this signal for compound **1** requires further investigation. Additional narrow lines in the spectrum of compound **2** (marked with asterisks in Fig. 4, *b*) belong to mononuclear copper complexes, which are present in the sample in trace amounts (the integrated intensity of these lines is negligible).

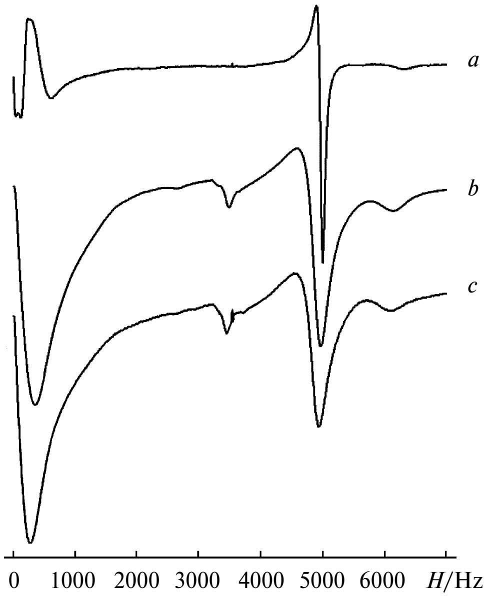

Fig. 3. X-band EPR spectra of polycrystalline samples of the copper complex $[py_2Cu_2(piv)_4]$ (*a*) and compounds **1** (*b*) and **2** (*c*) at room temperature.

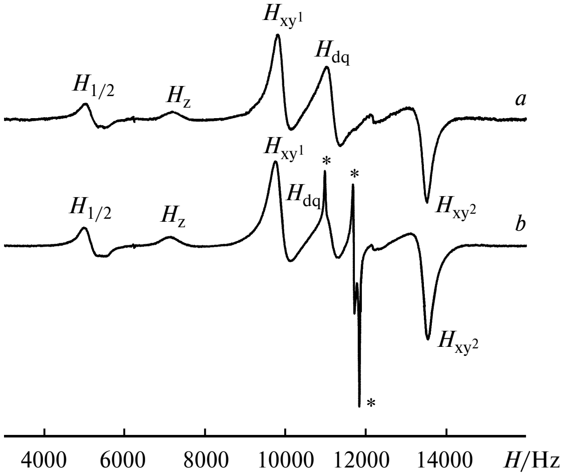

Fig. 4. Q-band EPR spectra (34.092 GHz) of polycrystalline samples of compounds **1** (*a*) and **2** (*b*) at room temperature.

The spin Hamiltonian for two interacting spins takes the following form:

$$H = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + D(S_z^2 - 1/3\, S(S+1)).$$

The solution of this Hamiltonian allowed us to determine the parameters of the spin Hamiltonian for compound **1**:

$$g_{\parallel} = 2.38, g_{\perp} = 2.07, D = 0.368 \text{ cm}^{-1},$$

and the spin Hamiltonian for compound **2**:

$$g_{\parallel} = 2.38, g_{\perp} = 2.07, D = 0.374 \text{ cm}^{-1}.$$

A comparison of the EPR spectra of compounds **1** and **2** (Fig. 3, *b*, *c*) with the EPR spectrum of the dinuclear copper complex $[py_2Cu_2(piv)_4]$ (Fig. 3, *a*) showed that the absorption lines in the EPR spectra of compounds **1** and **2** are broader than those observed for the compound $[py_2Cu_2(piv)_4]$. Apparently, this is associated with the larger number of copper atoms in the molecules and the presence of different spin-spin exchange channels in multispin architectures.

To sum up, we showed that the reaction of copper nitrate with potassium 1,1-cyclohexanediacetate affords the 1D polymer $\{[(EtOH)_2Cu_2(CHDAA)_2] \cdot EtOH\}_n$ (**1**). The addition of pyridine as the *N*-donor ligand to the starting reaction mixture inhibits the formation of the polymer, thus initiating the formation of the heterometallic octadecanuclear architecture $[K_2(\eta^1\text{-}H_2O)_6(\eta^1\text{-py})_8Cu_{16}(\eta^1\text{-}OH)_2(\mu_4\text{-}CHDAA)_{16}] \cdot EtOH \cdot MeCN \cdot 3H_2O$ (**2**), in which the dianion $(\eta^1\text{-}H_2O)_6(\eta^1\text{-py})_8Cu_{16}(\eta^1\text{-}OH)_2(\mu_4\text{-}CHDAA)_{16}$ serves as a metal-containing macropolycyclic ligand.

Experimental

The complexes were synthesized in air with the use of purified solvents. New compounds were synthesized with the use of $Cu(NO_3)_2 \cdot 3H_2O$ (analytical grade), $CuCl_2 \cdot 2H_2O$ (high-purity grade), pyridine (analysis grade, Acros organics), 1,1-cyclohexanediacetic acid (Alfa Aesar), potassium hydroxide (analytical grade), and tetrabutylammonium hydroxide (40% solution in methanol, Appli Chem). The salts K_2CHDAA and $(NBu_4)_2CHDAA$ were synthesized by the neutralization of 1,1-cyclohexanediacetic acid with KOH and NBu_4OH, respectively. The X-band EPR spectra were measured on a Bruker Elexsys E-680X radiospectrometer and the Q-band EPR spectra were obtained on a Bruker Elexsys E-580 spectrometer at room temperature. The IR spectra were recorded on a Specord M-80 instrument in KBr pellets. The microanalysis was carried out on a Carlo Erba analyzer.

Poly[bis(μ_4-1,1-cyclohexanediacetato-*O,O´,O´,O″*)bis(ethanol)dicopper(II)], solvate with an ethanol molecule, $\{[(EtOH)_2Cu_2(\mu_4\text{-}(OOC)_2CH_2(C_6H_{10})CH_2)_2] \cdot EtOH\}_n$ (1). The compound K_2CHDAA (0.229 g, 0.83 mmol) was dissolved with heating (60 °C) in ethanol (20 mL), and then $Cu(NO_3)_2 \cdot 3H_2O$ (0.2 g, 0.83 mmol) was added. The reaction mixture was stirred with heating for 1 h. The resulting pale-green precipitate was filtered off. Toluene (10 mL) was added to the resulting green-blue solution. The solution was concentrated to 10 mL and kept at room temperature for 10 h. The emerald-green crystals suitable for X-ray diffraction were washed with cold ethanol (0 °C) and dried in air at 20 °C. The yield of compound **1** was 0.095 g (34.8% based on the starting amount of copper). Found (%): C, 43.79; H, 6.54. $C_{26}H_{46}Cu_2O_{11}$. Calculated (%): C, 47.19; H, 7.01. IR (KBr), ν/cm^{-1}: 2924 s, 2852 m, 1616 s, 1561 w, 1548 w, 1528 w, 1424 s.br, 1316 w, 1284 w, 1232 w, 1128 v.w, 1088 w, 1048 m, 828 m, 880 m, 860 m, 800 w, 732 m, 688 w, 596 w, 472 w, 420 w.

Bis(η^1-hydroxo)hexadecakis(μ_4-1,1-cyclohexanediacetato-*O,O´,O´,O″*)hexakis(η^1-aqua)octakis(η^1-pyridine)hexadecacopper(II)dipotassium, solvate with one acetonitrile molecule, three water molecules, and one ethanol molecule, $[K_2(\eta^1\text{-}H_2O)_6(\eta^1\text{-py})_8Cu_{16}(\eta^1\text{-}OH)_2(\mu_4\text{-}(OOC)_2CH_2(C_6H_{10})CH_2)_{16}] \cdot EtOH \cdot MeCN \cdot 3H_2O$ (2). Method *A*. The compound K_2CHDAA (0.229 g, 0.83 mmol) was dissolved with heating (t = 60 °C) in ethanol. Then $Cu(NO_3)_2 \cdot 3H_2O$ (0.20 g, 0.83 mmol) was added to the hot solution, and the mixture was stirred for 10 min until a green-blue solution and a green precipitate formed. Then pyridine (0.14 mL, 1.66 mmol) was added to the reaction mixture, and the mixture was stirred with heating (60 °C) for 90 min. The solution was filtered off from the poorly soluble green precipitate, acetonitrile (10 mL) was added, and the mixture was concentrated to 5 mL and kept at –5 °C for 48 h. A mixture of emerald-green rhombic crystals suitable for X-ray diffraction and a green fine-crystalline precipitate was separated from the solution by decantation, washed with cold ethanol (–5 °C), and dried in air. The yield of compound **2** was 0.019 g (5% based on the starting amount of copper). Found (%): C, 46.55; H, 5.80; N, 2.10. $C_{204}H_{293}Cu_{16}K_2N_9O_{76}$. Calculated (%): C, 47.28; H, 5.70; N, 2.43. IR (KBr) ν/cm^{-1}: 3435 s.br, 2924 s, 2853 s, 1615 s, 1537 w, 1486 w, 1448 m, 1414 s, 1385 m, 1314 w, 1282 w, 1216 w, 1185 w, 1152 w, 1070 w, 1037 w, 848 w, 805 w, 754 w, 731 w, 698 m, 626 w, 562 w, 476 w, 427 w.

Method *B*. Ethanol (40 mL) was added to a mixture of H_2CHDAA (0.2203 g, 1.10 mmol) and a 40% tetrabutylammonium hydroxide solution (1.4246 g, 2.20 mmol of NBu_4OH), and the reaction mixture was stirred at 40 °C until H_2CHDAA was completely dissolved. Then K_2CHDAA (0.0202 g, 0.073 mmol) was added, and the reaction mixture was stirred until the reagent was completely dissolved. The salt $CuCl_2 \cdot 2H_2O$ (0.2 g, 1.173 mmol) or $Cu(NO_3)_2 \cdot 3H_2O$ (0.283 g, 1.173 mmol) was added to the resulting solution, the mixture was stirred for 5 min, and then pyridine (0.186 g, 2.347 mmol) was added. The reaction mixture was stirred with heating (50 °C) for 1 h. The emerald-green solution was filtered off from the poorly soluble pale-green precipitate. Acetonitrile (10 mL) was added to the resulting solution. The solution was concentrated to 15 mL and kept at room temperature for 2 h. The emerald-green rhombic crystals that formed

Table 1. Crystallographic characteristics for complexes **1** and **2**

Compound	**1**	**2**
Molecular formula	$C_{26}H_{46}Cu_2O_{11}$	$C_{204}H_{293}Cu_{16}K_2N_9O_{76}$
Molecular weight	661.71	5182.31
Crystal system	Triclinic	Tetragonal
Space group	$P\bar{1}$	$P4/n$
a/Å	10.320(2)	24.8207(13)
b/Å	12.501(3)	24.8207(13)
c/Å	13.001(2)	19.8403(11)
α/deg	110.626(4)	90
β/deg	101.170(4)	90
γ/deg	93.891(5)	90
V/Å	1523.0(5)	12223.0(11)
Z	4	2
ρ_{calc}/g cm^{-3}	1.443	1.408
μ/cm^{-1}	1.450	1.475
θ_{min}—θ_{max}-Scan-range/deg	2.71—26.01	1.94—26.40
$T_{min/max}$	0.6384/0.8928	0.6339/0.8428
Number of measured reflections	6170	72406
Number of reflections with $I > 2\sigma(I)$	5838	12386
R_1[a]	0.0729	0.0743
wR_2[b]	0.1080	0.1827

Note. [a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

(the formation of a fine-crystalline precipitate was not observed) were separated from the solution by decantation, washed with cold ethanol (−5 °C), and dried in air. The crystals thus obtained were suitable for X-ray diffraction. The yield of compound **2** was 0.1830 g (48.1% based on the starting amount of copper). Found (%): C, 46.49; H, 5.85; N, 2.06. $C_{204}H_{293}Cu_{16}K_2N_9O_{76}$. Calculated (%): C, 47.28; H, 5.70; N, 2.43. IR (KBr), ν/cm^{-1}: 3435 s.br, 2924 s, 2853 s, 1615 s, 1537 w, 1486 w, 1448 m, 1414 s, 1385 m, 1314 w, 1282 w, 1216 w, 1185 w, 1152 w, 1070 w, 1037 w, 848 w, 805 w, 754 w, 731 w, 698 m, 626 w, 562 w, 476 w, 427 w.

X-ray diffraction study. The X-ray diffraction data sets for complexes **1** and **2** were collected using the standard technique[14] on an automated Bruker SMART APEX II diffractometer equipped with a CCD detector and a monochromated radiation source (MoKα, λ = 0.71073 Å). For both complexes, semiempirical absorption corrections were applied.[15] The structures of the complexes were solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for all nonhydrogen atoms. The hydrogen atoms of the *tert*-butyl substituents of the pivalate ligands were positioned geometrically and refined using a riding model. All calculations were carried out with the use of the SHELX97 program package.[16] The crystallographic parameters and the structure refinement statistics are given in Table 1. Taking into account the disorder of the solvent, the X-ray diffraction data were corrected using the squeeze option of the PLATON program.[17]

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