Thermal decomposition of dinuclear complexes $LM(\mu-OOCR)_4ML$ (L is α -substituted pyridine).

2.* Influence of α-amino groups on the nature of the thermolysis products of Mn^{II}, Fe^{II}, Co^{II}, and Cu^{II} pivalates**

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The solid-state thermal decomposition of the dinuclear pivalate complexes $LM(\mu-OOCR)_4ML$, both those synthesized earlier $(M = Mn^{II}, Fe^{II}, or Co^{II}; L = 2,6-(NH_2)_2C_5H_3N)$ and new complexes $(M = Cu^{II}; L = 2,6-(NH_2)_2C_5H_3N)$ or $(2-NH_2)(6-CH_3)C_5H_3N)$, was studied by differential scanning calorimetry and thermogravimetry. The decomposition of the Co^{II} complexes is accompanied by the aggregation to form the volatile octanuclear complex $Co_8(\mu_4-O)_2(\mu_n-OOCCMe_3)_{12}$ (n = 2 or 3), whereas the thermolysis of the Mn^{II} , Fe^{II}, and Cu^{II} complexes is destructive, the phase composition of the decomposition products being substantially dependent on the nature of metal and the α substituent R in the apical organic ligand.

Key words: tetrabridged dinuclear manganese, iron, cobalt, and copper pivalate complexes, 2,6-diaminopyridine, 2-amino-6-methylpyridine, solid-state thermal decomposition, X-ray diffraction study, magnetic properties.

In the previous paper,¹ we have demonstrated that the nature of α -substituted pyridine L (in particular, the α substituent R) in the dinuclear tetracarboxylate complexes $LM(\mu$ -OOCBu^t)₄ML (M = Ni or Cu) has a substantial effect on the products of the solid-state thermal (20–400 °C) decomposition of the complexes. For example, in the case of α -R = Me (in 2,3-dimethylpyridine), the thermal decomposition of the nickel complex produces nickel metal only, whereas the thermolysis of the analogous copper complex affords a mixture of products, *viz.*, CuO, Cu₂O, and copper metal. This is a substantial difference from the situation observed for quinoline derivatives (CH group of the conjugated benzene ring is in the α position) or complexes with pyridine² (α -R = H, for the nickel complex), which readily eliminate L in the

early thermolysis steps. The final degradation affords oxides CuO or NiO, respectively. The related manganese and iron complexes generate only metal oxides regardless of their composition. The thermolysis of the corresponding dinuclear cobalt pivalates affords the volatile octanuclear cluster $Co_8(\mu_4-O)_2(\mu_2-Piv)_6(\mu_3-Piv)_6$ already in the early steps of heating.^{1,3} Taking into account the observed effects, there were reasons to expect that the thermal decomposition of these complexes can be controlled by varying the nature of the apical ligands. In the present study, we investigated the thermal decomposition of dinuclear pivalate complexes with NH2-substituted pyridine ligands. It is known^{4,5} that the NH_2 group is easily oxidized and can formally serve as an inner-sphere reducing agent or can be involved in condensation reactions. The choice of the ligand was also based on the known data on the thermolysis of methylhydrazine complexes of 3d metals yielding⁶ metals or even alloys (upon the combined thermolysis of the complexes) at rather low temperatures (lower than 400 °C).

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Results and Discussion

Earlier, we have synthesized^{7,8} the dinuclear tetrabridged manganese(II) and iron(II) pivalate complexes $[(NH_2)_2C_5H_3N]_2M_2(\mu - OOCCMe_3)_4 \cdot 4MeCN$ (M = Mn (1) or Fe (2)) with the apical diaminopyridine ligands by the reaction of the $[(EtOH)Mn(OOCBu^{t})_{2}]_{n}$ or $[Fe(OOCBu^{t})_{2}]_{n}$ polymers with 2,6-diaminopyridine (L¹) in acetonitrile. These complexes contain MeCN solvent molecules, which form hydrogen bonds with the protons of the amino groups in the α positions of the pyridine ligand. These compounds proved to be rather stable under argon as opposed to the nickel and cobalt complexes, which were immediately transformed into amidine complexes in the presence of acetonitrile.⁹ The dinuclear cobalt-containing analog of complexes 1 and 2, $[(NH_2)_2C_5H_3N]_2Co_2(\mu$ -OOCCMe₃)₄ (3), was synthesized in dichloromethane (as the solvate with two CH₂Cl₂ molecules),¹⁰ whereas attempts to synthesize the related nickel complex failed.

Synthesis of aminopyridine-containing copper(II) pivalates

Since the copper(II) complex with L¹ was unknown, we synthesized this compound by the reaction of the $[Cu(OOCBu^{t})_{2}]_{n}$ polymer (4)¹¹ with this ligand using the ratio Cu : L¹ = 1 : 1. The reaction of 4 with 2,6-diaminopyridine (L¹) in inert benzene produced the $[(NH_{2})_{2}C_{5}H_{3}N]_{2}Cu_{2}(\mu$ -OOCCMe₃)₄ complex (5) as the solvate with one benzene molecule in virtually quantitative yield. According to the X-ray diffraction study, the distance between the copper atoms in antiferromagnetic complex 5 (μ_{eff} = 1.920 (260 K)-0.171 μ B (5 K)) is 2.762(1) Å (Fig. 1), which is longer than the corresponding distances in the dinuclear fragments $Cu_{2}(\mu$ -OOCCMe₃)₄ of the starting polymer 4 (Cu...Cu, 2.580 Å).¹¹ The ligand molecule is coordinated in a monodentate fashion through the pyridine nitrogen atom

(Cu-N, 2.243(3) Å), the N-Cu...Cu-N fragment being virtually linear (N-Cu...Cu angle, 178.8(3)°). The presence of intramolecular hydrogen bonding is an important structural feature of complex 5. Since donor solvent molecules are absent in the crystal structure of complex 5, the protons of the α -amino groups interact with the oxygen atoms of the bridging pivalate ligands (N-H...O, 2.109–2.197 Å; N-H...O angles, 145–151°). This is formally indicative of the possibility of the chemical interaction between these ligands in the course of thermal decomposition of the complex. It appeared that no radical changes are observed upon the replacement of diaminopyridine L¹ by the ligand containing one amino group, viz., 2-amino-6-methylpyridine (L²). Thus, the reaction of **4** with L^2 in benzene (Cu : $L^2 =$ 1:1, 80 °C) produces the dinuclear complex $[(2-NH_2)(6-Me)C_5H_3N]_2Cu_2(OOCBu^t)_4$ (6) in virtually quantitative yield.

According to the X-ray diffraction study, the distance between the copper atoms in molecule **6** is 2.730(1) Å (Fig. 2), which is somewhat shorter than the corresponding distance in complex 5, although the Cu-N (apical ligand) distance (2.296(3) Å) is slightly longer than the corresponding distance in diamine complex 5. The N-Cu...Cu-N fragment is also virtually linear (N-Cu...Cu angle, 177.14(7)°) like that in 2,6-diaminopyridine-containing analog 5. In complex $\mathbf{6}$, there is intramolecular hydrogen bonding between the hydrogen atoms of the *trans*-amino groups of two ligands L^2 and the oxygen atoms of the bridging *trans*-pivalate anions (N-H...O, 2.200–2.515 Å; N–H...O angles, 127–144°). Therefore, it can be noted that the dinuclear structures of complexes 5 and 6 are additionally stabilized by intramolecular hydrogen bonding with the involvement of the apical ligands.

An attempt to prepare an analog of complex 5, *viz.*, the dinuclear copper complex, in which the amino



Fig. 1. Structure of complex 5.



Fig. 2. Structure of complex 6.

groups are involved in hydrogen bonding with an external solvating agent, for example, with acetonitrile (as was observed in manganese and iron compounds 1 and 2), led to an unexpected result. It appeared that the reaction of copper polymer 4 with L^1 in MeCN under an inert atmosphere produces green cocrystals of the antiferromagnetic compound { $[(NH_2)_2C_5H_3N]_2Cu_2(OOCBu^t)_4$. • $(CH_3CN)_2Cu_2(OOCBu^t)_4$] • $2CH_3CN$ (7) (Fig. 3) as a solvate with two acetonitrile molecules (7.2CH₃CN), $\mu_{eff} = 2.693 \,\mu_B \,(300 \text{ K}) - 0.120 \,\mu_B \,(2 \text{ K})$, in nearly quantitative yield in spite of the ratio L^1 : $Cu_{at} = 1$: 1. According to the X-ray diffraction study, the crystal structure of 7 consists of two different centrosymmetric dinuclear complexes, viz., the target diaminopyridine complex $[(NH_2)_2C_5H_3N]_2Cu_2(OOCBu^t)_4$ (7a) (analog of 5) and the dinuclear complex $(CH_3CN)_2Cu_2(OOCBu^t)_4$ (7b), which is apparently generated in the step of dissolution of polymer 4 in MeCN. The Cu...Cu distance between the copper atoms in complex 7a is 2.7059(7) Å, which is shorter than that observed in compound 5 (Cu...Cu, 2.7621(11) Å) but is somewhat longer than that in 7b (Cu...Cu, 2.6349(8) Å; Cu-N, 2.209(3) Å; N-Cu...Cu

angle, 173.03(8)°). The Cu–N distance in **7a** (2.273(3) Å) is slightly longer than that in **5**, although the N–Cu...Cu–N fragment remains linear (N–Cu...Cu angle, 177.82(8)°). Apparently, this effect is, to some extent, associated with the presence of additional hydrogen bonding between the protons of the α -amino groups and the nitrogen atoms of the acetonitrile solvent molecules (N–H...NCMe, 2.26(2) Å) in the crystal structure of **7a**, resulting in the "pushing off" of the L–Cu fragment from the dimetal tetracarboxylate core. As opposed to complex **7a**, this binding is absent in complex **7b**, as well as in complex **5**, in which, on the contrary, intramolecular hydrogen bonding and the tightening effect are observed.

Thermal decomposition of dinuclear aminopyridine-containing Mn, Fe, Co, and Cu pivalate complexes. In a search for ways of using coordination compounds as molecular precursors of ultrathin films (including nanosized structures),^{12,13} it is of particular interest to investigate the mild thermolysis of dinuclear tetrapivalates with 3d metal atoms, which are readily soluble in organic solvents and contain ligands serving as potential reducing agents for metals. This process holds promise for preparing ultrathin



Fig. 3. Structure of the $\{[(NH_2)_2C_5H_3N]_2Cu_2(OOCBu^t)_4 \cdot (CH_3CN)_2Cu_2(OOCBu^t)_4\} \cdot 2CH_3CN \text{ cocrystalline complex (7).}$

metal films at moderate temperatures (≤ 400 °C), due to which it can compete with the known^{14,15} energy-consuming electrochemical methods. For this purpose, we studied the thermolysis of molecular precursors, *viz.*, aminopyridine-containing Mn^{II}, Fe^{II}, Co^{II}, and Cu^{II} pivalate complexes, which can be synthesized in virtually quantitative yields.

The thermolysis of the diaminopyridine manganese and iron pivalate complexes [(NH₂)₂C₅H₃N]₂M₂(µ-OOCCMe₃)₄ · 4MeCN (M = Mn(1) or Fe(2)) was found to proceed similarly to the thermolysis of their analogs with lutidine.¹ The thermolysis of 1 and 2 starts with the hydrogen bond cleavage and the removal of the acetonitrile solvent molecules ($\Delta_{evap}H = 29.7 \text{ kJ mol}^{-1}$, $t_{evap} =$ 82 °C)¹⁶ in two steps accompanied by energy absorption (50-108 °C, 128.5±3.5 kJ mol⁻¹ for 1; 50-113 °C, 132 ± 3.5 kJ mol⁻¹ for 2) (Fig. 4). It can be seen that the thermal effects for both compounds are equal within experimental error. After elimination of the solvent molecules, the product melts without decomposition ($t_{melt} =$ 111.0±1.0 °C, $\Delta_{\text{melt}}H = 38.5\pm3.0 \text{ kJ mol}^{-1}$ for 1; $t_{\text{melt}} =$ 115.0±1.0 °C, $\Delta_{\text{melt}}H = 47.5\pm3.0 \text{ kJ mol}^{-1}$ for 2). The melting point and the enthalpy of melting for the ironcontaining complex are somewhat higher than those for the manganese complex. The first decomposition step of dinuclear tetrabridged complexes 1 and 2 proceeds in the temperature ranges of 148–290 °C and 160–315 °C and is accompanied by the endotherms of 138.0 ± 4.0 kJ mol⁻¹

and 154.5 ± 4.0 kJ mol⁻¹ and the weight loss of $24.2\pm1.0\%$ and $24.4\pm1.0\%$, respectively. It is likely that the neutral coordinated diaminopyridine ligand is eliminated and a new structure, presumably, with the composition $[M(\mu-OOCCMe_3)_2]_n$, starts to form in this temperature range;¹ however, the step of formation of a stable intermediate was not observed for **2**. In the case of **1**, the temperature range of the existence of the corresponding intermediate is rather narrow.

The last thermolysis step (310-485 °C and 315-500 °C for 1 and 2, respectively) is accompanied by a complex-shaped thermal effect. In this step, the weight loss is $39.6\pm1.0\%$ and $39.1\pm1.0\%$ for 1 and 2, respectively. The total weight loss is $81.9\pm1.5\%$ and $81.7\pm1.5\%$ for complexes 1 and 2, respectively. According to the X-ray powder diffraction analysis, the thermolysis affords mixed-valence oxides Mn_3O_4 and Fe_3O_4 , respectively, as the final products (Table 1).

Unlike manganese and iron complexes **1** and **2**, the cobalt compound $[(NH_2)_2C_5H_3N]_2Co_2(\mu$ -OOCCMe₃)₄• • 2CH₂Cl₂ (**3**) contains two dichloromethane solvent molecules. The preliminary thermolysis step of **3** (42–80 °C) is accompanied by the endotherm $\Delta H = 58.5\pm4.5$ kJ mol⁻¹, and the weight loss is 19.2±1.0% (Fig. 5). Apparently, this effect corresponds to the removal of the solvent molecules (for CH₂Cl₂, $\Delta_{vap}H = 28.06$ kJ mol⁻¹, the boiling point is 40±1 °C).¹⁶ At temperatures above 80 °C, the unsolvated dimer is formed. For this dimer,



Fig. 4. Temperature dependences of the heat flux change (Q) (a, b) and the weight loss (m) (c, d) for complexes 1 (a, c) and 2 (b, d).

Characteristics	1*	2*	3	5*	6*	7*
Boiling point	285	285	285	285	208	285(L1) 81(MeCN)
M—N bond length/Å	2.179	2.157-2.169	2.109	2.243(3)	2.296(3)	2.273(3) (L1) 2.209(3) (MeCN)
Number of steps	2	2	2	1	1	2
Temperature of the onset of decomposition/°C	148	160	165	139	128	115
Temperature range/°C						
step I	148-290	160-315	165-230	139-400	128-400	115-140
step II	290-310	**	**	***	***	150-400
step III	310-485	315-500	230-300	***	***	***
Temperature of cessation	485	510	230	400	400	400
of decomposition/°C						
Final decomposition product	Mn ₃ O ₄	Fe ₃ O ₄	$\operatorname{Co}_8(O)_2(\operatorname{piv})_{12}$	Cu	Cu	Cu, Cu ₂ O

Table 1. Characteristics of the decomposition of dinuclear tetrabridged cobalt complexes 1-3 and 5-7

* Decomposition after the removal of the solvate solvent.

** Was not virtually isolated.

*** The steps of melting of the complex, the removal of the coordinated ligand, and the complete degradation of the metal core were not distinguished in the temperature dependence of the weight loss.



Fig. 5. Temperature dependences of the heat flux change (a) and the weight loss (b) for complex 3.

step I (165–230 °C) is accompanied by melting with decomposition ($t_{melt} = 164\pm1$ °C). The total thermal effect of this step is 122.0±6.5 kJ mol⁻¹, and the weight loss is 22.5±1.5%. Step II of the thermolysis of **3** was not distinguished. In step III (230–300 °C), the weight loss is 52.3±1.5%. The total weight loss is 94.0±1.5% (residue is 6.0% of the initial weight). Hence, the observed situation is typical of other dinuclear cobalt pivalate complexes.^{2,17} At temperatures of about 230 °C, the highly volatile octanuclear cluster $Co_8(\mu_4-O)_2(\mu_2-piv)_6(\mu_3-piv)_6$ is formed, and it is readily removed from the reaction zone.² This compound is the major final thermolysis product.

The main effects of the α -amino substituents in the thermal decomposition of pivalate dimers are observed for complexes 5–7 containing copper(II) atoms. This electron-rich metal has a rather high oxidation potential.

In the course of decomposition of diaminopyridine complex 5, the first thermolysis step involves the intramolecular hydrogen bond cleavage in the temperature range of 40–70 °C. After the removal of the benzene solvent molecules (75–120 °C), individual decomposition steps are virtually indistinguishable. The decomposition starts at temperatures above 139 °C, the onset of decomposition being accompanied by melting (first endotherm) (Fig. 6, *a* and *c*). The further deep decomposition proceeds in a wide temperature range from 139 to 400 °C and is accompanied by a complex endotherm. In this temperature range, the weight loss is $81.2\pm2.0\%$. The phase composition of the solid final decomposition product determined by the X-ray powder diffraction method (Table 2)



Fig. 6. Temperature dependences of the heat flux change (Q) (a, b) and the weight loss (m) (c, d) for complexes 5 (a, c) and 6 (b, d).

shows that copper metal is the only decomposition product.

No principal differences in the thermolysis of methylaminopyridine complex **6** and diaminopyridine complex **5** were observed. The first decomposition step of complex **6** also involves the intramolecular hydrogen bond cleavage in the temperature range of 40–80 °C. The decomposition starts at temperatures above 128 °C, the onset of decomposition also being accompanied by melting (first endotherm) (see Fig. 6, *b* and *d*). The deep decomposition proceeds in a wide temperature range from 128 to 400 °C and is accompanied by a complex endotherm. In this temperature range, the weight loss is $83.2\pm2.0\%$. The phase composition of the solid final decomposition product determined by X-ray powder diffraction (see Table 2) shows that copper metal is the only decomposition product.

The decomposition of the cocrystals of $\{[(NH_2)_2C_5H_3N]_2Cu_2(OOCBu^t)_4 \cdot (CH_3CN)_2Cu_2(OOCBu^t)_4\} \cdot 2CH_3CN$ (7) involves the removal of the acetonitrile

Decomposition product of 5		Decomposition product of 6		Decomposition product of 7		Cu [4-836]*		Cu ₂ O [5-667]*	
d∕Å	I/I_0 (%)	$d/\text{\AA}$	I/I_0 (%)	$d/\text{\AA}$	I/I_0 (%)	$d/{ m \AA}$	I/I_0 (%)	$d/{ m \AA}$	I/I_0 (%)
				2.463	40			2.465	100
				2.130	5			2.135	37
2.090	100	2.085	100	2.092	100	2.088	100		
1.805	60	1.807	50	1.810	50	1.808	46		
				1.510	5			1.510	27
1.278	50	1.278	30	1.279	10	1.278	20		

Table 2. X-ray powder diffraction analysis of the solid decomposition products of compounds 5-7

*Powder Diffraction File, Swarthmore: Joint Committee on Powder Diffraction Standards.



Fig. 7. Temperature dependences of the heat flux change (a) and the weight loss (b) for complex 8.

solvent molecules at the first step (68-101 °C); the weight loss is $6.3\pm2.0\%$. At temperatures above 101 °C, unsolvated cocrystals exist. For this compound, the weight loss in step I (115–140 °C) is $5.9\pm1.0\%$. In this case, the onset of decomposition is not accompanied by melting as opposed to complexes 1-3, 5, and 6 (Fig. 7). In this temperature range, the coordinated acetonitrile molecules are apparently removed from the dinuclear complex $(CH_3CN)_2Cu_2(OOCBu^t)_4$ (7b). This suggestion is confirmed by the weight loss (percentage of two acetonitrile molecules is 5.68%). Step II of decomposition (>150 °C) occures in a wide temperature range (150-400 °C) and is accompanied by energy changes. In step II, the weight loss is 70.1 \pm 1.5%. The total weight loss is 82.3 \pm 1.5%. The phase composition of the solid final decomposition product determined by the X-ray powder diffraction method (see Table 2) shows that the decomposition affords only a mixture of copper metal and copper(I) oxide in a ratio of ~ 2 : 1.

The appearance of Cu_2O among the thermolysis products of complex 7 is, apparently, attributed to the presence of acetonitrile compound 7b involved in cocrystals 7. At the same time, the presence of complex 7a containing the diaminopyridine ligand in cocrystals 7 promotes the formation of copper metal and is, presumably, responsible for the absence of copper(π) oxide, which is formed upon thermolysis of Cu^{II} pivalates with quinoline and lutidine¹ or upon decomposition of Cu₂(OOCBu^t)₄ \cdot \cdot (HOOCBu^t)₂ and polymer 4.¹⁸ In our opinion, these results open possibilities for the directed formation of films (including multilayer films) starting from dinuclear 3d metal pivalates as molecular precursors. In this case, it is necessary to vary only the nature of the apical ligand, which presents no serious difficulties.

Experimental

All synthetic operations were carried out under pure argon with the use, if necessary, of deaerated or anhydrous solvents using the standard Schlenk technique. The starting pivalates $1,^7$ $2,^8$ and 4 (see Ref. 19) were synthesized according to procedures described earlier. The synthesis of new compounds was carried out with the use of trimethylacetic acid (Acros Organics), 2,6-diaminopyridine (Acros Organics), and 2-amino-6-methylpyridine (Merck-Schuchardt).

The IR spectra were recorded on a Specord M-80 spectrophotometer in KBr pellets. The elemental analysis of compounds **5–11** was carried out on a Carlo Erba C, H, N analyzer in the Center of Collaborative Research of the N. S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences. The magnetic susceptibility of compound **5** · C₆H₆ was measured on a SQUID MPMS-59 Quantum Design magnetometer in the temperature range of 2–300 K. The effective magnetic moments were calculated by the equation $\mu_{eff} = (8\chi_M T)^{1/2}$.

The thermal decomposition of compounds 1-3 and 5-7was studied by differential scanning calorimetry (DSC) and thermogravimetry (TG) on DSC-20 and TG-50 units of a Mettler TA-3000 thermoanalyzer. Samples of compounds 1-3 and 5-7 were heated under dry argon at a constant rate of 5 deg min⁻¹. For each compound, two DSC experiments and three TG experiments were performed. The weight loss upon thermal degradation was determined directly on the TG-50 unit; the accuracy of weighing was $\pm 2 \cdot 10^{-3}$ mg. The thermal decomposition was studied in steps by DSC, which involved the division of the total temperature range into intervals. The size and number of these intervals were determined based on the overall pattern of the weight loss upon decomposition. This approach allowed us to determine the weight loss in each temperature range and compare the results of DSC with the TG data. The results of these methods were in satisfactory agreement, which confirms the reliability of the experimental data. The accuracy of the determination of anomalous points and thermal effects in the DSC curves was $\pm 1^{\circ}$ and $\pm 0.5\%$, respectively.

The X-ray powder diffraction analysis of the decomposition products was carried out on a FR-552 monochromator chamber (CuK_{α 1} radiation) using germanium as the internal standard (X-ray diffraction patterns were processed on an IZA-2 comparator with an accuracy of ± 0.01 mm) and with the use of the STOE Powder Diffraction System.

Synthesis of complexes

Complex $Co_2[2,6-(NH_2)_2C_5H_3N]_2(\mu_2-OOCCMe_3)_4$ • 2CH_2Cl_2 (3 • 2CH_2Cl_2) (see Ref. 10). Dichloromethane (35 mL)was added to the [Co(OOCCMe_3)_2]_n polymer (0.5 g, 1.92 mmol;

per formula unit Co(OOCCMe₃)₂) and 2,6-diaminopyridine (0.209 g, 1.92 mmol), and the reaction mixture was stirred at 35 °C for 10 min until the reagents were completely dissolved. The solution was concentrated at 0.1 Torr and 20 °C to 10 mL and kept at 5 °C for 12 h. Green crystals that precipitated were separated by decantation, washed with cold dichloromethane, and dried under a stream of argon. The solvate of compound 3 with two CH₂Cl₂ molecules was obtained in a yield of 0.83 g (95% based on the starting amount of cobalt) Found (%): C, 41.81; H, 6.03; 9.34. Co₂C₃₂H₅₄Cl₄N₆O₈. Calculated (%): C, 42.18; H, 5.93; N, 9.23. IR (KBr), v/cm⁻¹: 3490 m, 3360 m, 3420 s, 3236 w, 2960 s, 2868 s, 2814 m, 2336 m, 1636 s, 1612 v.s, 1592 v.s, 1536 m, 1484 s, 1460 s, 1456 v.s, 1420 v.s, 1376 m, 1360 v.s, 1308 s, 1268 s, 1228 s, 1176 s, 1104 w, 1028 w, 936 w, 896 m, 788 v.s, 776 s, 728 m, 696 m, 668 w, 608 v.s, 476 m, 424 w, 404 s, 308 m.

The crystals were used for the X-ray diffraction study.

Bis(2,6-diaminopyridino)tetra(μ_2 -O,O'-trimethylacetato)dicopper(11), $Cu_2[2,6-(NH_2)_2C_5H_3N]_2(\mu_2-OOCCMe_3)_4 \cdot C_6H_6$ $(5 \cdot C_6 H_6)$. Benzene (30 mL) was added to polymer 4 $[Cu(OOCCMe_3)_2]_n$ (0.331 g, 1.169 mmol; per formula unit $Cu(OOCCMe_3)_2$) and 2,6-diaminopyridine (0.136 g, 1.169 mmol), and the reaction mixture was stirred at 80 °C for 20 min until the reagents were completely dissolved. The solution was concentrated at 0.1 Torr and 20 °C to 15 mL and kept at ~20 °C for 24 h. The green crystals that precipitated were separated by decantation, washed with cold benzene, and dried in air. The solvate of compound 5 with one benzene molecule was obtained in a yield of 0.5 g (96% based on the starting amount of copper). Found (%): C, 52.29; H, 6.34; N, 10.09. C₃₆H₅₆Cu₂N₆O₈. Calculated (%): C, 52.22; H, 6.82; N, 10.15. IR (KBr), v/cm^{-1} : 3492 s, 3472 s, 3376 s, 3256 m, 3232 m, 3176 w, 3148 w, 2980 m, 2960 m, 1636 s, 1616 s, 1596 v.s, 1484 s, 1468 s, 1420 s, 1376 m, 1364 m, 1308 m, 1228 m, 1180 w, 1116 w, 1064 w, 1032 w, 992 w, 900 w, 788 m, 728 w, 692 m, 624 w, 520 w, 448 w, 420 w, 388 w, 356 w, 316 w.

The crystals were used for the X-ray diffraction study.

Bis(2-amino-6-methylpyridino)tetra(μ_2 -0,0'-trimethylacetato)dicopper(II), $[(2-NH_2)(6-CH_3)C_5H_3N]_2Cu_2(OOCBu^t)_4$ (6). Benzene (30 mL) was added to polymer 4 $[Cu(OOCCMe_3)_2]_n$ $(0.3 \text{ g}, 1.129 \text{ mmol}; \text{ per formula unit } Cu(OOCCMe_3)_2)$ and 2-amino-6-methylpyridine (0.122 g, 1.129 mmol), and the reaction mixture was stirred at 80 °C for 20 min until the reagents were completely dissolved. The solution was concentrated at 0.1 Torr and 20 °C to 15 mL and kept at ~20 °C. Green crystals that precipitated were separated by decantation, washed with cold benzene, and dried in air. Compound 6 was obtained in a yield of 0.41 g (96% based on the starting amount of copper). Found (%): C, 51.86; H, 7.34; N, 7.26. C₃₂H₅₂Cu₂N₄O₈. Calculated (%): C, 51.39; H, 7.01; N, 7.49. IR (KBr), v/cm⁻¹: 3444 m, 3368 m, 3320 m, 2964 s, 2908 m, 2864 m, 1696 m, 1668 m, 1636 s, 1616 s, 1600 s, 1540 m, 1516 m, 1480 s, 1456 s, 1416 s, 1375 m, 1356 m, 1276 w, 1260 m, 1224 s, 1192 w, 1172 w, 1096 m, 1028 m, 936 w, 896 m, 884 w, 868 w, 800 m, 788 m, 732 w, 716 w, 668 w, 624 m, 600 w, 552 w, 532 w, 444 w, 436 w, 400 w, 388 w, 356 w, 312 w.

The crystals were used for the X-ray diffraction study.

Cocrystals of bis(2,6-diaminopyridino)tetra(μ_2 -0,0'-trimethylacetato)dicopper(11) and bis(acetonitrilo)tetra(μ_2 -0,0'-trimethylacetato)dicopper(11), {2,6-(NH₂)₂C₅H₃N]₂(μ_2 -OOCCMe₃)₄·(CH₃CN)₂Cu₂(μ_2 -OOCCMe₃)₄·2CH₃CN) (7·2CH₃CN). Acetonitrile (40 mL) was added to polymer 4 [Cu(OOCCMe₃)₂]_n (0.331 g, 1.169 mmol; per formula unit Cu(OOCCMe₃)₂) and 2,6-diaminopyridine (0.136 g, 1.169 mmol), and the reaction mixture was stirred at 80 °C for 10 min until the reagents were completely dissolved. The solution was concentrated at 0.1 Torr and 20 °C to 25 mL and kept at ~5 °C for 24 h. Green crystals that precipitated were separated by decantation, washed with cold acetonitrile, and dried in air. Crystals of compound 7 with two acetonitrile molecules were obtained in a yield of 0.798 g (89% based on the starting amount of copper). Found (%): C, 48.44; H, 6.35; N, 9.36.

Parameter	5	6	7
Molecular formula	C ₃₆ H ₅₆ Cu ₂ N ₆ O ₈	C ₃₂ H ₅₂ Cu ₂ N ₄ O ₈	C ₅₈ H ₉₂ Cu ₄ N ₁₀ O ₁₆
Molecular weight	827.95	747.86	1439.58
Space group	<i>P</i> 6(5)	Triclinic, $P\overline{1}$	Triclinic, P1
a/Å	12.4581(14)	9.5206(10)	11.2647(6)
b/Å	12.4581(14)	10.8447(10)	11.8627(6)
c/Å	48.519(6)	11.0699(10)	15.6881(8)
α/deg	90	62.067(10)	99.5010(10)
β/deg	90	72.395(10)	72.395(10)
γ/deg	120	83.133(10)	110.8230(10)
$V/Å^3$	6521.5(13)	962.16(16)	1878.73(17)
Ζ	6	1	1
$\rho_{calc}/g \text{ cm}^{-3}$	1.265	1.291	1.272
μ/mm^{-1}	1.0291	1.764	1.180
Radiation	Mo-K α ($\lambda = 0.71073$ Å)	Cu-K α ($\lambda = 1.5418$ Å)	
θ-2θ-Scan range/deg	1.89-28.00	4.71-74.91	2.13-29.56
Number of measured reflections	12787	5807	19440
Number of reflections with $I > 2\sigma(I)$	5401	3875	9290
R_1	0.0574	0.0452	0.0543
wR_2	0.1165	0.1260	0.0937

Table 3. Crystallographic parameters of complexes 5–7

 $C_{58}H_{92}Cu_4N_{10}O_{16}.$ Calculated (%): C, 48.39; H, 6.44; N, 9.73. IR (KBr), v/cm^{-1}: 3472 s, 3380 s, 3264 m, 3168 w, 3180 w, 2960 s, 2932 s, 2904 m, 2868 m, 2828 w, 1644 s, 1612 s, 1596 s, 1484 s, 1468 s, 1420 s, 1376 s, 1364 m, 1308 m, 1260 w, 1224 s, 1180 m, 1120 w, 1072 w, 1032 w, 988 w, 940 w, 896 m, 788 s, 756 w, 728 m, 668 w, 620 s, 540 w, 500 w, 444 m, 412 m, 400 w, 388 m, 316 m.

The crystals were used for the X-ray diffraction study.

X-ray diffraction study. X-ray reflections for complexes 5 and 6 were measured on an automated Bruker P-4 (graphitemonochromated λ Mo-K α) and Enraf-Nonius CAD-4 (graphitemonochromated λ Cu-K α) diffractometers, respectively; for complex 7; on an automated Bruker AXS SMART 1000 diffractometer (graphite-monochromated λ Mo-K α , 250 K) equipped with a CCD detector according to a standard procedure.²⁰ Semiempirical absorption corrections were applied.²¹ The crystallographic parameters and the refinement statistics for the structures of 5–7 are given in Table 3.

The structures of all 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 and the pyridine rings in the coordinated amine molecules were positioned geometrically and refined using a riding model. All calculations were performed with the use of the SHELX97 program package.²²

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