



Thermodynamic properties of tetrabridged binuclear copper complexes with apical substituted pyridine ligands

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ABSTRACT

Heat capacities of six synthesized complex compounds with apical substituted pyridine ligands were studied by adiabatic calorimetry (AC), differential scanning calorimetry (DSC), and computer simulation. Thermodynamic properties were calculated from experimental heat capacity data and by computer simulation. It was shown that below the structural phase transition temperatures the lattice component of heat capacity has the similar values for all studied complexes and above this temperature structural changes are determined by the nature of apical ligand.

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1. Introduction

The practical use of metal complexes as molecular precursors for the preparation of epitaxial or protective insulating coatings, the low-temperature synthesis of high-melting-point compounds and alloys, the purification of metals, and many other purposes evidently requires, in addition to the data on the chemical, mechanical, and adsorption properties of these compounds, a knowledge on the temperatures of their phase and chemical transformations (melting, sublimation, and decomposition), the saturated vapor pressure, and chemical stability in the presence of particular gaseous or solid compounds. As a rule, the thermodynamic data necessary for the determination of such technological characteristics are lacking.

Binuclear VII and VIII Group 3d transition metal complexes with four bridging pivalate ligands, which have the composition $LM(\mu\text{-OOCMe}_3)_4ML$ (L is substituted pyridine) and are soluble in organic solvents, are well known. Due to the rather simple synthesis, these compounds would be of considerable practical use. The synthesis and structures of representatives of this class of compounds containing Co(II) [1–3] and Ni(II) [4,5] atoms have been studied in sufficient detail. Recently, the synthesis of complexes with Fe(II) and Mn(II) atoms has also been reported [6].

In the present study, we investigated tetrabridged dinuclear copper complexes with apical substituted pyridine ligands having the composition $LCu(\mu\text{-OOCMe}_3)_4CuL$ (L = pyridine derivatives, such as quinoline (C₉H₇N) (1), 2,3-dimethylpyridine (2,3-(CH₃)₂C₅H₃N) (2), 2,6-diaminopyridine (2,6-(NH₂)₂C₅H₃N) (3), 2-amino-6-methylpyridine (2-NH₂)(6-CH₃)C₅H₃N) (4), 2-aminopyridine ((2-NH₂)C₅H₄N) (5), and 3-aminopyridine ((3-NH₂)C₅H₄N) (6)). The synthesis and structures of the complexes have been described previously [7,8], and the nature of substituted pyridine L has been shown to have a substantial effect on the products of solid-state thermal (293–700 K) decomposition of the complexes. The data on the thermodynamic properties of this class of compounds were hitherto lacking.

The aim of the present study was to investigate the thermodynamic properties and phases transitions of this series of dinuclear copper pivalates in the condensed phase and to calculate the thermodynamic functions of the pivalate (C₉H₇N)Cu(μ-OOCMe₃)₄Cu(C₉H₇N) in the gas phase.

2. Experimental

2.1. Synthesis of complexes

The complexes $LCu(\mu\text{-OOCMe}_3)_4CuL$ (L = quinoline (1), 2,3-dimethylpyridine (2), 2,6-diaminopyridine (3), 2-amino-6-methylpyridine (4), 2-aminopyridine (5), and 3-aminopyridine

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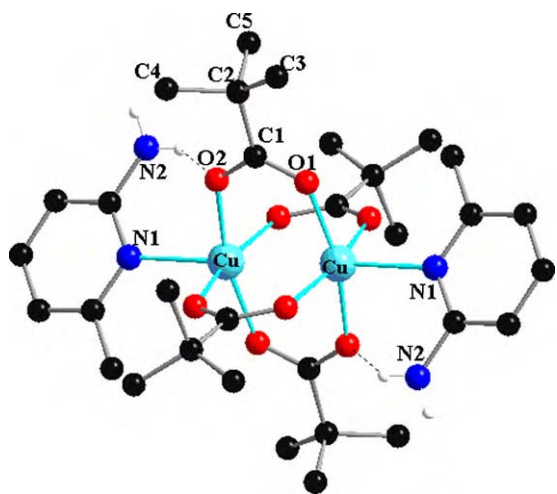


Fig. 1. Molecular structure of the complex $\text{LCu}(\mu\text{-OOCMe}_3)_4\text{CuL}$ (**4**; L=2-amino-6-methylpyridine).

(**6**) were synthesized according to known procedures and characterized by magnetic measurements, elemental analysis, IR spectroscopy, and X-ray diffraction [7,8] (Fig. 1).

Compounds **1–6** are bright-green crystalline compounds. According to the X-ray diffraction data, complexes **3** and **5** crystallize as solvates with one benzene molecule per formula unit. For differential scanning calorimetry (DSC) measurements, solvent molecules were removed from the crystals of complexes **3** and **5** by heating to 400 K directly in the measuring cell.

2.2. Method of determination of thermodynamic properties in the condensed phase

Experimental measurements of the isobaric heat capacity by differential scanning calorimetry and the corresponding calculations were carried out using the ASTM E1269-95 standard test method. The experimental data were processed with the use of the NETZSCH Proteus Thermal Analysis software described in detail elsewhere [9].

The heat capacity was measured in special aluminum containers ($V=56\text{ mm}^3$, $d=6\text{ mm}$) with a hole in a lid (the ratio of the surface area of the bottom of the cell to the surface area of the hole was about 36). The samples were weighted with an accuracy of 10^{-2} mg . The average weight of the samples was about 10 mg. The measurements were carried out on a NETZSCH 204 F1 instrument in a dry argon flow (10 ml min^{-1}) at a heating rate of 10 K min^{-1} . The temperature calibration of the instrument was carried out with the standard ISO/CD 11357-1 based on the phase transition points of reference compounds (C_6H_{12} , Hg, KNO_3 , In, Sn, Bi, CsCl; 99.99% purity). Synthetic sapphire ($m=12.69\text{ mg}$) was used as a standard for the heat flow calibration. For each sample, at least three series of measurements were carried out.

The influence of the thermal history of the sample on the characteristics of thermal anomalies was studied by varying the rates of cooling and heating from 3 to 30 K min^{-1} . The parameters of the anomalies were determined using the standards ISO/CD 11357-1 and ISO/CD 11357-2. The anomalous entropy was determined by the graphical integration of the experimental curve $C_p(T)/T$.

The heat capacity was measured by adiabatic calorimetry on a BKT-3 calorimetric low-temperature adiabatic apparatus designed and manufactured in the TERMIS LLC. The measurements were carried out in an automatic mode using a system consisting of a computer and an analog data control and processing unit. Samples were placed in a thin-walled titanium cylindrical container with an inner volume of 1 cm^3 . The container was sealed in a special chamber under a helium atmosphere at a pressure of about

30 kPa. The temperature of the calorimeter was measured with an iron–rhodium resistance thermometer. The sensitivity of the temperature-measuring system was 10^{-3} K ; the sensitivity of the analog-to-digital converter was $0.1\text{ }\mu\text{V}$. The energy equivalent of the calorimeter was determined by measuring the heat capacity of the empty tube filled with gaseous helium under a pressure of 8.5 kPa. To verify the measurement procedure, we determined the heat capacity of benzoic acid (K-2 grade) as the reference. The measurements showed that the error of heat capacity measurements at helium temperatures is $\pm 2\%$, decreases to $\pm 0.4\%$ as the temperature increases to 40 K, and is $\pm 0.2\%$ in the range of 40–350 K. The construction of the apparatus and the measurement procedure have been described in detail previously [10].

The calculations were carried out with the use of the tabulated atomic weights [11].

The experimental data obtained by adiabatic calorimetry were smoothed by Eq. (1) [12,13]

$$C_p^0(T) = a_0 T C_V^2 + n \left[\frac{1}{3} \sum_{j=1}^3 a_j D_j \frac{\theta_j}{T} + a_4 E \frac{\theta_E}{T} + a_5 K \left(\frac{\theta_L}{T}, \frac{\theta_U}{T} \right) \right] \quad (1)$$

where n is the number of atoms in the molecule of the complex, D and E are the Debye and Einstein functions, respectively, K is the Kieffer K function [14], $\theta_1, \theta_2, \theta_3, \theta_E, \theta_L$, and θ_U are the characteristic temperatures, a_0, a_1, a_2, a_3, a_4 , and a_5 are linear coefficients. The first term of the equation $a_0 T C_V^2$ corresponds to the contribution of the lattice expansion. The parameters a_0 – a_5 and θ_1 – θ_U were determined by the non-linear least squares. The calculation procedure has been described in detail earlier [15]. Eq. (1) was also used for calculations of the entropy, the enthalpy change, and the reduced Gibbs energy of the complexes.

The results of several series of DSC measurements were statistically processed. The deviation of the experimental points from the average value was smaller than 3% throughout the temperature range under study. The temperature contributions to the enthalpy and entropy $H^0(T) - H^0(0)$, $H^0(T) - H^0(T_1)$, and $S^0(T) - S^0(T_1)$ were evaluated by the graphical integration of the curves $C_p(T)$ and $C_p(T)/T$. The values of $H^0(T) - H^0(0)$ and the magnitudes of the entropy were calculated from the values of $H^0(298\text{ K}) - H^0(0)$ and $S^0(298\text{ K})$ obtained from adiabatic calorimetry data.

The heat capacities of complexes **3** and **5** without solvent molecules were calculated by the additive formula (2) from the experimental data obtained for the solvates:

$$C_p(\text{Cu}_2\text{Piv}_4\text{L}_2) = C_p^{\text{exp}}(\text{Cu}_2\text{Piv}_4\text{L}_2 \cdot \text{C}_6\text{H}_6) - C_p^{\text{lit}}(\text{C}_6\text{H}_6) \quad (2)$$

The heat capacity of benzene was taken from the publication [16]; the data were extrapolated to high temperatures by the function (3) proposed by Berman and Brown [17]

$$C_p(T) = k_0 + k_1 T^{-0.5} + k_2 T^{-2} + k_3 T^{-3} \quad (3)$$

and to low temperatures by the polynomial function (4) [18]

$$C_p(T) = \sum_i a_i C_{En} \left(\frac{\theta_i}{T} \right) \quad C_{En}(x) = x^2 \frac{\exp(x)}{[\exp(x) - 1]^2} \quad x = \frac{\theta}{T} \quad (4)$$

The contribution of the common core of the complexes to the heat capacity was evaluated by the additive formula (5):

$$C_p(\text{Cu}_2\text{Piv}_4) = C_p^{\text{exp}}(\text{Cu}_2\text{Piv}_4\text{L}_2) - 2C_p^{\text{lit}}(\text{L}) \quad (5)$$

In the calculations, the published data on the heat capacities of quinoline and 2,3-dimethylpyridine [19] were used. The heat capacities of the other ligands were estimated on the assumption that the substituent makes equal contributions to the heat capacities of benzene and pyridine, for example:

$$C_p(\text{C}_6\text{H}_5(\text{NH}_2)) - C_p(\text{C}_6\text{H}_6) = C_p(\text{C}_6\text{H}_4\text{N}(\text{NH}_2)) - C_p(\text{C}_6\text{H}_5\text{N}) \quad (6)$$

The validity of this estimate was confirmed by the results obtained for methyl derivatives of benzene and pyridine.

The regular part of the heat capacities of complexes **1** and **6** was determined by approximating the parts of the experimental curves, which are characterized by the monotonic temperature dependence of the heat capacity, by Eq. (3). The validity of the simultaneous data processing before and after the thermal anomalies was confirmed by the Fischer test. The anomalous part of the heat capacity of complex **6** was calculated as the difference between the experimental curve $C_p(T)$ and the regular contribution to the heat capacity.

2.3. Method of calculations of thermodynamic properties in the gas phase

In the present study, we performed statistical calculations of the thermodynamic functions of complex **1** in the gas phase. The molecular properties required for statistical calculations, such as the equilibrium configuration of the nuclear subsystem and the normal-mode vibrational frequencies, were described by the low-calculation-cost density functional theory (DFT) method, which gives reliable results [20,21]. The equilibrium configuration of the nuclear subsystem was sequentially calculated by the density functional theory with the use of the following functionals:

- P
B
1. E [22] with DZ2P basis sets [23] on all atoms.
P
B
2. E with TZ2P basis sets [24] on all atoms.
3. B3LYP [25] with TZVPP basis sets [24] on copper atoms and 6-311G** basis sets [26] on light atoms. In the latter case, the choice of the corresponding basis sets was determined by the parameterization of the B3LYP functional and the data available in the literature [20].

It was found that the most reliable results were obtained with the use of the B3LYP exchange-correlation functional combined with triple-zeta basis sets.

The Hessian was also calculated by the density functional theory with the use of the B3LYP functional and the above-mentioned basis sets. The calculations of normal-mode vibrational frequencies were preceded by the Hessian projection procedure [27] to exclude the contribution of the translational and rotational degrees of freedom.

The calculations at the B3LYP level of theory were carried out with the use of the PC Gamess version [28] and the Gamess US program package [29].

The thermodynamic functions were calculated using the OpenThermo program [30].

The sums over states were calculated in the rigid rotor-harmonic oscillator (RRHO) approximation. The rotational sums over states at all temperatures were calculated by the direct summation of the quantum levels. Before the statistical calculations, the calculated frequencies were multiplied by the scaling coefficient of 0.98, which is commonly used in calculations at the B3LYP level of theory [21]. The vibrational sum over states was found to make the major contribution to the total sum over states. The zero-point correction was not included in the below-given calculated values of the thermodynamic functions. Its value was 2144.87 kJ mol⁻¹.

The presence of two paramagnetic centers (copper ions) in the complex leads to the appearance of the so-called exchange interaction, resulting in the existence of the low-lying excited state. In the case of a rather small splitting, the contribution of the excited state to the electronic sum over states can be substantial, which was taken into account. According to the results of investigation on

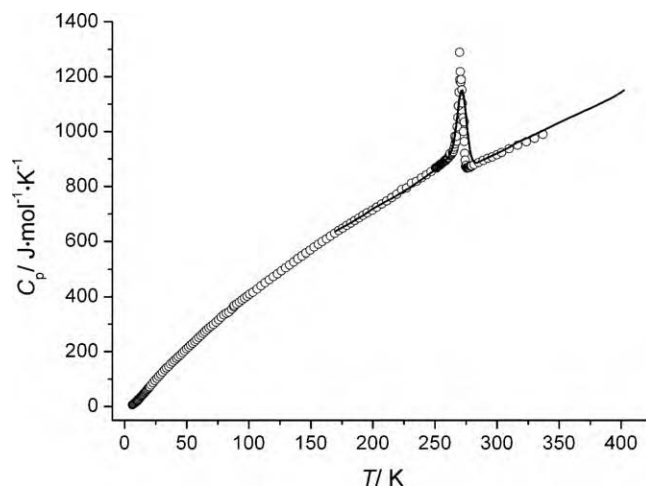


Fig. 2. Heat capacity of complex **1**: o adiabatic calorimetry data; — DSC data.

the temperature dependence of the magnetic susceptibility of this complex [8], the singlet state is the ground state, and the splitting between this state and the triplet state (the exchange interaction parameter) is 394 cm⁻¹. Based on these data, we took into account the contribution of the electronic sum over states calculated by the following equation:

$$Q_{el} = 1 + 3 \exp\left(-\frac{E(T) - E(S)}{RT}\right)$$

where the pre-exponential term 3 accounts for the triply-degenerate triplet state. All thermodynamic calculations were carried out in the ideal gas approximation. All thermodynamic functions were calculated under standard conditions (at one-atmosphere pressure).

3. Results and discussion

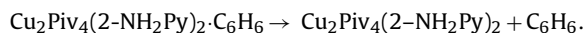
The experimental data and the results of their thermodynamic processing for complex **1** are presented in Table A.1 (see Appendix) and Fig. 2. It should be noted that the results obtained by two calorimetric methods are in satisfactory agreement.

The thermodynamic functions of complex **1** calculated in the ideal gas approximation in the 50–1000 K temperature range are given in Table A.2 (see Appendix).

For complexes **2–4**, the temperature dependence of the heat capacity was experimentally determined only by DSC (Tables A.3–A.5, see Appendix). As mentioned above, complex **5**, like complex **3**, crystallizes with one benzene solvent molecule.

The temperature dependence of the heat capacity of complex **5**·C₆H₆ was studied by adiabatic calorimetry and DSC (Table A.6 (see Appendix) and Fig. 3). The temperature dependence of the heat capacity of the solvate **5**·C₆H₆ (Fig. 2) shows an anomaly as a peak at $T_{max} = 335.2$ K.

To elucidate the nature of this anomaly, we performed DSC measurements for the same weighed sample after the first and repeated heating. A comparison of the DSC curves obtained after the first and repeated heating with the results of adiabatic calorimetry shows that this peak can be assigned to the decomposition of the solvate:



The TGA study of this sample of the complex with 2-aminopyridine showed that the heating of the complex to 400 K leads to the weight loss of 9.5 ± 0.5%, which is consistent with the theoretical content of benzene in the solvate **5**·C₆H₆ (9.8%), i.e., this effect is actually

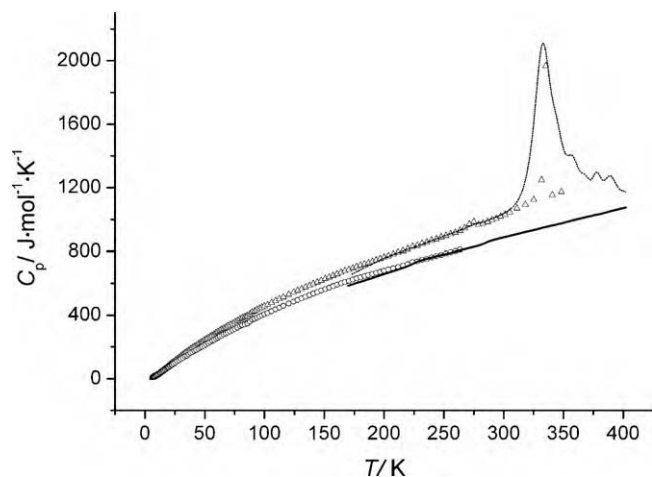


Fig. 3. Heat capacity of complex **5**: Δ , adiabatic calorimetry data for the solvate; \circ , the estimate of the heat capacity of the complex without solvent molecules from the adiabatic calorimetry data, the upper curve represents the experimental DSC data (first heating), the lower curve represents the experimental DSC data (second heating, the complex without solvent molecules).

associated with the removal of the solvent molecule from the complex.

The heat capacity of complex **5** without solvent molecules, which was calculated by the additive formula (2) from the experimental data obtained for the solvate $5 \cdot C_6H_6$ by adiabatic calorimetry, is in satisfactory agreement with the experimental data obtained by DSC (Table A.7). The heat capacity and the thermodynamic properties of unsolvated complex **3** were evaluated in a similar way based on the DSC data (Table A.4, see Appendix).

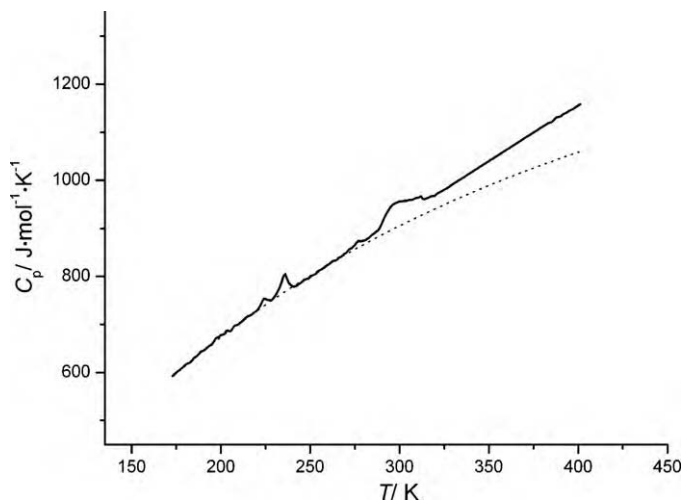


Fig. 4. Heat capacity of complex **6**: the experimental curve (solid line) and the regular part (dashed line).

Heat capacity and thermodynamic functions of complex **6** are given in Table A.8 (see Appendix) and Fig. 4.

An analysis of the temperature dependence of the isobaric heat capacity of the complexes under study showed two reproducible anomalies in the temperature ranges of 210–240 K and 260–290 K (Fig. 5, Table 1).

The first anomaly is pronounced for the complex $Cu_2Piv_4(3-NH_2Py)_2$ (**6**) (a doublet of peaks). In the dependence $C_p(T)$ for the complex $Cu_2Piv_4(C_9H_7N)_2$ (**1**), this anomaly is absent due, apparently, to steric hindrance caused by the bulky quinoline molecules. For the other complexes, this anomaly is manifested as a more

Table 1
Parameters of the anomalies of the complexes measured under standard experimental conditions.

No.	Method	$T_{\max/onset}$, K	T_{infl} , K	$\Delta H^{\circ}(T_{\max/onset})$, J mol ⁻¹	$\Delta S^{\circ}(T_{\max/onset})$, J K ⁻¹ mol ⁻¹	ΔC_p° , J K ⁻¹ mol ⁻¹
The first anomaly						
1	AC, DSC	Absent				
2	DSC	–	≈ 230 – 240	–	–	no reliable measurements
3			≈ 240 – 250			
4			233 ± 4			
5	AC	≈ 220	–	no reliable measurements		–
6	DSC	222.4	–	–	–	–
		–	224 ± 7	–	–	18 ± 5
		220 ± 1	–	263 ± 41	1.32 ± 0.19	–
The second anomaly						
1	AC	270.0	–	4760	19.72	–
2	DSC	Absent				
3		Absent				
4		–	≈ 260 – 275	–	–	no reliable measurements
5	AC	275.0	–	248	0.77	–
		–	284 ± 1	–	–	14 ± 4
6	DSC	289	–	670 ± 420	2.1 ± 1.4	–
		–	289 ± 3	–	–	17 ± 6

T_{onset} is the temperature of the onset of the process corresponding to the first peak according to the DSC data, T_{\max} is the temperature of the maximum according to the adiabatic calorimetry data, T_{infl} is the temperature of devitrification (inflection point) based on the DSC data.

Table 2
Geometric parameters of the hydrogen bonding in complexes 1–6.

D...A	Parameters			DHA angle (°)
	Distance (Å)			
	D–H	H...A	D...A	
Compound 1 ^a quinoline	–	–	–	–
Compound 6 ^b 3-diaminopyridine	0.860	2.415–2.580	3.024–3.086	117.46–128.29
Compound 2 ^a lutidine	0.930, 0.960	2.40(3)–2.71(3)	3.140(6)–3.390(6)	107.00, 141.00
Compound 4 ^b 2,6-methylaminopyridine	0.860	2.200, 2.515	2.940, 3.110	127.03, 144.02
B compound 5 ^b 2-diaminopyridine	0.880	2.075–2.240	2.889–3.014	143.09–153.35
Compound 3 ^b 2,6-diaminopyridine	0.860	2.109–2.197	2.891–2.949	145.90–151.10

^a C–H...O.

^b N–H...O.

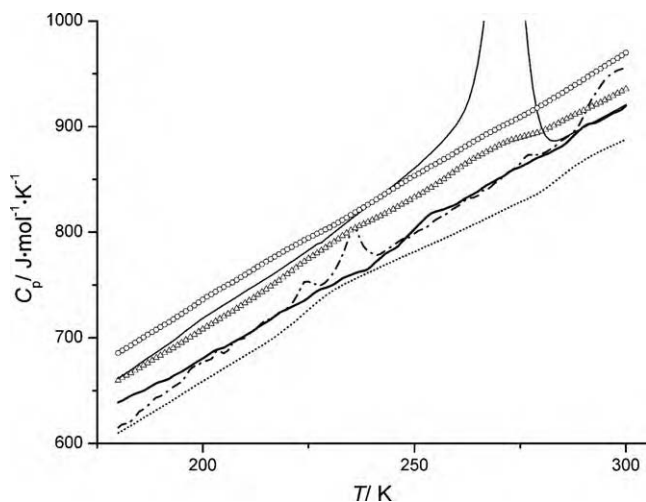
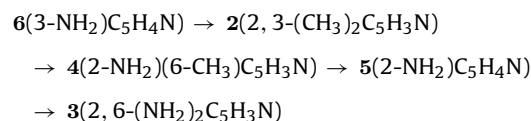


Fig. 5. Fragments of the DSC curves of the complexes: 1, thin line; 2, circles; 3, thick line; 4, triangles; 5, dashed line; 6, dash-dotted line.

or less pronounced S-shaped inflection. An analysis of the X-ray diffraction data [7,8,31] for the complexes under study suggested that the anomaly is associated with the fact that the rotational degrees of freedom (bending vibrations) of substituted pyridine molecules freeze out. The phase that exists before the anomaly is a “conformational” glass. The hindrance of rotation of aminopyridine at low temperatures is apparently attributed to intra- and intermolecular hydrogen bonding between the hydrogen atoms of the amino groups and the oxygen atoms of the carboxylate bridges (Fig. 1). The hydrogen bonds in the complexes are very weak, because the hydrogen and oxygen atoms are rather distant from each other (although the distances between these atoms are smaller than the sum of their van der Waals radii). The low binding energy accounts for the possibility of a strong weakening of these bonds at relatively low temperatures (about 230 K). The energy barrier to rotation of substituted pyridines in the complexes increases in the following series:



The weaker the hydrogen bonds between the ligand and the core of the complex, the stronger the anomaly. In the phase after the anomaly, the corresponding degrees of freedom freeze out (Table 2).

The second anomaly is absent in the curves for complexes 2 (2,3-(CH₃)₂C₅H₃N) and 3 (2,6-(NH₂)₂C₅H₃N). For complex 1 (C₉H₇N), the anomaly is manifested as a peak, whose parameters are independent of the thermal history of the sample; for the other samples

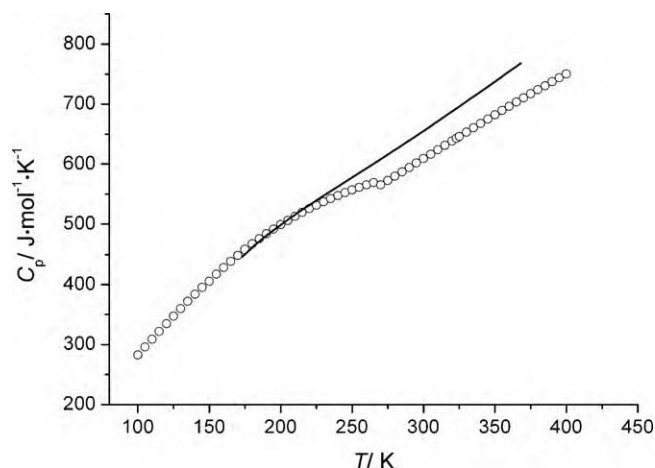


Fig. 6. Heat capacity of the fragment Cu₂Piv₄: the estimate from the regular part of the heat capacity, which was calculated from the simultaneously processed experimental results of adiabatic calorimetry and DSC for complex 1, is represented by circles; the estimate from the experimental DSC data for complex 2 is represented by a solid line.

(4–6), the anomaly appears as an S-shaped inflection. The anomaly is associated with the rotation of the *tert*-butyl fragments about the C–C axis. In complex 1, this rotation leads to the appearance of two equally probable orientations, is accompanied by structural changes, and results in the appearance of a peak in the DSC curve. In complexes 4–6, the *tert*-butyl groups show bending vibrations, and the anomaly appears as an S-shaped inflection in the DSC curve.

Before the first anomaly, the heat capacity of the complexes is well described by the additive formula (Eq. (5)), which is indicative of the similar values of its lattice component (Table 3, Fig. 6). Once the inner rotation freezes out, the additive formula gives unsatisfactory results, which is quite understandable because the rotational component of the heat capacity substantially depends on the energy barrier. This is well illustrated by complexes 5 and 6. The energy barrier to rotation about the N–C bond in 2-aminopyridine is substantially higher due to the stronger hydrogen bonding between the proton of the NH₂ group and the nearest oxygen atoms of the pivalate anion.

Table 3
Estimates of the contribution of the fragment Cu₂Piv₄ to the heat capacity of complexes 1–6.

No.	1	2	3	4	5	6
T (K)			210			
Method	AC		DSC		AC	AC
C _p (J mol ⁻¹ K ⁻¹)	520	520	516	520	525	525
T (K)			323			
Method			DSC			
C _p (J mol ⁻¹ K ⁻¹)	640	696	645	699	641	687

4. Summary

To sum up, as a result of the study of tetrabridged pivalate complexes with substituted pyridines as apical ligands, we obtained the temperature dependences of the heat capacity, calculated the thermodynamic properties from the experimental data, and showed that the lattice component of the heat capacity has similar values for all complexes up to the temperature of structural changes. Above this temperature, the structural changes are determined by the nature of the apical ligand.

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The calculations were carried out on a MFTI-60 cluster in the Department of Nanotechnologies and Informatics of the Moscow Institute of Physics and Technology (State University).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tca.2010.06.004](https://doi.org/10.1016/j.tca.2010.06.004).

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