

# Coordination Diversity in Mono- and Oligonuclear Copper(II) Complexes of Pyridine-2-Hydroxamic and Pyridine-2,6-Dihydroxamic Acids

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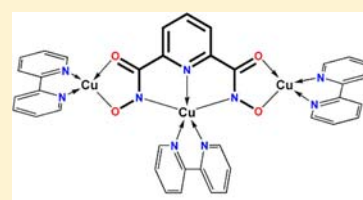
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## S Supporting Information

**ABSTRACT:** Solution and solid state studies on Cu(II) complexes of pyridine-2-hydroxamic acid (HPicHA) and pyridine-2,6-dihydroxamic acid (H<sub>2</sub>PyDHA) were carried out. The use of methanol/water solvent allowed us to investigate the Cu(II)–HPicHA equilibria under homogeneous conditions between pH 1 and 11. In agreement with ESI-MS indication, the potentiometric data fitted very well with the model usually reported for copper(II) complexes of  $\alpha$ -aminohydroxamate complexes ( $[\text{CuL}]^+$ ,  $[\text{Cu}_3(\text{LH}_{-1})_4]^{2+}$ ,  $[\text{CuL}_2]$ ,  $[\text{CuL}_2\text{H}_{-1}]^-$ ), however with much higher stability of the 12-MC-4 species. A series of copper(II) complexes has been isolated in the solid state and characterized by a



variety of spectroscopic methods, X-ray structure analysis, and magnetic susceptibility measurements. The ligands show the tendency to form bi- and trinuclear species with copper(II) ions due to the  $\{(N,N'); (O,O')\}$  bis-(bidentate) chelating-and-bridging mode involving  $(O,O')$ -hydroxamate chelate formation combined with  $(N,N')$  chelating with participation of the pyridine and hydroxamic nitrogen atoms, so that the hydroxamate groups play a  $\mu_2$ -( $N,O$ )-bridging role. Molecular and crystal structures of three synthesized complexes  $[\text{Cu}_3(\text{PicHA-H})_2(\text{dipy})_2](\text{ClO}_4)_2 \cdot 4/3\text{DMSO} \cdot 2/3\text{H}_2\text{O}$  (**1**),  $[\text{Cu}_2(\text{PyDHA})-(\text{dipy})_2](\text{ClO}_4)_2 \cdot \text{DMF} \cdot \text{H}_2\text{O}$  (**4**), and  $[\text{Cu}_3(\text{PyDHA-2H})(\text{tmeda})_3](\text{ClO}_4)_2$  (**5**) (dipy, 2,2'-dipyridyl; tmeda,  $N,N,N',N'$ -tetramethyl-1,2-diaminoethane) have been determined by single crystal X-ray analysis. In **1**, two trans-situated doubly deprotonated hydroxamic ligands play a  $\{(O,O')(N,N')\}$ -(bis)bidentate-bridging function forming bridges between the medial, Cu(2) ( $\text{CuN}_4$ ), and the terminal, Cu(1) and Cu(3) ( $\text{CuN}_2\text{O}_2$ ), copper(II) ions; the chelating dipy ligands are coordinated to the latter. In **4**, the ligand is coordinated in a classical  $(O,O')$ -hydroxamate chelating mode with the help of two separate hydroxamic groups while the central tridentate donor compartment remains vacant. In **5**, the hydroxamate ligand is coordinated by the  $\{(O,O'); (N,N',N''); (O'',O''')\}$ -tridentate-(bis)bidentate mode, bridging three copper(II) ions, while the chelating tmeda ligands are coordinated to all three copper(II) ions. Magnetic susceptibility measurements (1.7–300 K) of powdered samples of the trinuclear complexes **1** and **5** revealed strong antiferromagnetic coupling between the copper(II) ions mediated by the hydroxamate bridges.

## INTRODUCTION

Hydroxamic acids are important chelating ligands ubiquitous in coordination and analytical chemistry and chemical biology.<sup>1</sup> During the past two decades, hydroxamic acids revealed their potential also as versatile bridging ligands capable of forming various polynuclear complexes with elaborate topology, which has elicited a considerable growth in interest in their further applications in coordination chemistry, molecular magnetism, and supramolecular chemistry.<sup>1,2</sup> The ability to form alternative modes of bridging coordination has been successfully used for the synthesis of discrete oligonuclear compounds.<sup>1,2</sup> Although among hydroxamate polynuclear complexes the most well-known are metallacrowns (MC),<sup>1f,2c,e,f</sup> the bridging coordination of hydroxamates often gives discrete oligonuclear compounds with alternative molecular topologies<sup>2a,d</sup> and

coordination polymers.<sup>2g-i</sup> Proper functionalization of hydroxamic acid with other binding moieties can prevent the formation of metallacrowns and, instead, result in discrete oligonuclear complexes of nonmetallacrown topology. Note that metallacrowns can be formed only by the hydroxamic acids functionalized in the  $\alpha$ ,  $\beta$ , or  $\gamma$  position with respect to the hydroxamic function.<sup>1f,2c,e,f,3</sup>

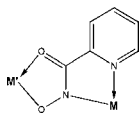
*o*-Picolinehydroxamic acids are good examples of  $\alpha$ -functionalized hydroxamates which are able to bridge metal ions and form various polynuclear species. Pyridine-2-hydroxamic acid, HPicHA, has been successfully used for one-step preparation of heteronuclear 15-MC-5 complexes, with copper(II), nickel(II),

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and zinc(II) ions forming a macrocyclic framework and diverse metal ions occupying the center of the metallacrown cavity: Cu(II)/Gd(III) or Eu(III),<sup>4</sup> Cu(II)/Pb(II), Hg(II), Ag(I) or Na(I),<sup>5</sup> Ni(II)/lanthanide(III) and Ni(II)/Pb(II),<sup>6</sup> and Zn(II)/lanthanide(III).<sup>7</sup> Moreover, planar copper(II) 15-MC-5 complexes of **HPicHA** were used as selective molecular recognition agents able to sequester uranyl(2+) ions in aqueous solution.<sup>8</sup> Although **HPicHA** forms with the Cu(II) 12-MC-4 complex,  $[\text{Cu}_5(\text{PicHA-H})_4]^{2+}$ , its thermodynamic stability in solution has not been determined due to solubility problems.<sup>9</sup> We have demonstrated that its degradation led to the formation of tetranuclear compounds which are the first examples of solely hydroxamate-based Cu(II) collapsed metallacrown complexes.<sup>9</sup> However, **HPicHA** was also shown to form other, non-metallacrown, polynuclear complexes. In particular, crystallization of the  $[\text{Cu}_5(\text{PicHA-H})_4]^{2+}$  complex in the presence of pyridine led to a destruction of the metallacrown core and formation of a trinuclear compound of  $[\text{Cu}_3(\text{PicHA-H})_2(\text{Py})_5(\text{NO}_3)_2]$  composition, with the hydroxamate coordinated *via* the  $\{(N,N'); (O,O')\}$  bis(chelate)-bridging mode (Scheme 1).<sup>10</sup> The same mode of bridging coordination of *o*-

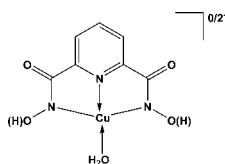
**Scheme 1.**  $\{(N,N'); (O,O')\}$ -Bis(bidentate) Coordination Mode of Pyridine-2-hydroxamate acid (**HPicHA**)



picolinehydroxamate has been recently reported by Griffith et al.<sup>11</sup> in a dinuclear platinum(II) complex,  $[\{cis\text{-Pt}(\text{NH}_3)_2\}_2(\mu\text{-PicHA-H})(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}]$ .

As far as pyridine-2,6-dihydroxamic acid, **H<sub>2</sub>PyDHA**, is concerned, its donor properties with respect to 3D-metal ions were, to the best of our knowledge, a subject of only one detailed study. Several years ago, a paper describing solution complexation equilibria of Cu(II)/Ni(II)–**PyDHA** systems was published.<sup>12</sup> While Ni(II) complexes were rather soluble in water, Cu(II) had to be studied in a high excess of ligand, as a decrease of metal-to-ligand molar ratio even down to 1:2 resulted in a complex precipitation above pH 4.12 It has been shown that among known dihydroxamates, **H<sub>2</sub>PyDHA** was the most effective ligand for Cu(II) and Ni(II) ions. The presence of a very strong trinitrogen chelating donor set brought about realization of the tridentate  $\{2N(\text{hydroxamate}), N(\text{Py})\}$  coordination mode, both in 1:1 and 1:2 complexes present in a wide range of pH (Scheme 2). However, Griffith et al.<sup>13</sup> have proposed realization of an alternative bis- $\{(O,O'); (O'',O''')\}$ -chelate mode in a ternary ruthenium(III) complex of **H<sub>2</sub>PyDHA** and edta. Although in the mentioned paper only the mononuclear complexes were presented, from the

**Scheme 2.** Trinitrogen Bis(chelate) Coordination Mode of **H<sub>2</sub>PyDHA** in Mononuclear Copper(II) Complexes Observed in Solution [16] and Isolated Complexes 2 and 3



molecular structures proposed it was evident that they contain vacant (O, O') donor sets clearly able to bind extra metal ions. Unfortunately, isolation of Cu(II) or Ru(III) complexes of **H<sub>2</sub>PyDHA** was unsuccessful. Recently, Griffith et al.<sup>14</sup> reported that reactions of **H<sub>2</sub>PyDHA** with platinum(IV), palladium(IV), and ruthenium(III) resulted in unexpected reduction of Pt(IV) and Pd(IV) ions, accompanied by hydrolytic decomposition of the latter with a formation of coordinated 2,6-dipicolinate.

Encouraged by the diversity of coordination modes and stoichiometries of *o*-picolinehydroxamate complexes, we have continued the research, and in this paper we report on a series of mono-, bi-, and trinuclear copper(II) complexes of **HPicHA** and **H<sub>2</sub>PyDHA**, their formation in solution, isolation, and detailed structural, spectral, and magnetochemical characterization. The general synthetic approach leading to the polynuclear compounds envisaged use of a rather high metal-to-ligand ratio, precluding MC formation, and additionally the introduction of blocking bidentate chelating ligands such as dipy and tmeda, able to saturate vacant positions of central metal ions.

## EXPERIMENTAL SECTION

**Materials and Physical Measurements.** All chemicals were commercial products of reagent grade and were used without further purification. Hydroxamic acids were synthesized accordingly to the reported methods.<sup>15</sup> Elemental analysis was conducted by the Microanalytical Service of the University of Wrocław. IR spectra (KBr pellets) were recorded on a Perkin-Elmer 180 Spectrometer in the range of 200–4000  $\text{cm}^{-1}$ . Absorbance and diffuse-reflectance spectra were collected on Beckman DU 650 and Beckman UV 5240 spectrophotometers, respectively. Electrospray (ESI) mass spectra were collected on a Finigan TSQ 700 mass spectrometer. Methanol or methanol/water (1:1) solutions were used to dissolve complexes with concentrations of  $10^{-4}$  to  $10^{-6}$  M. Magnetic data were measured with a Quantum-Design MPMS-5S SQUID magnetometer at 0.2 and 0.5 T in the range from 2 to 295 K. The powdered samples were contained in a gel bucket and fixed in a nonmagnetic sample holder. Diamagnetic corrections of the constituent atoms were calculated from Pascal's constants<sup>16</sup> and found to be  $-505 \times 10^{-6}$  (1),  $-439 \times 10^{-6}$  (4), and  $-456 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  (5) per 3 (1), 2 (4), and 3 (5) mol of copper(II) ions. Experimental susceptibilities were also corrected for the temperature-independent paramagnetism of  $60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  per Cu(II) and the magnetization of the sample holder. EPR spectra were obtained using a Bruker Elexsys E 500 spectrometer equipped with an NMR teslameter (ER 036TM) and frequency counter (E 41 FC) at the X-band.

**Speciation Studies.** The solution studies were carried out in a MeOH/H<sub>2</sub>O (80:20 w/w) mixture, using doubly distilled water. The solution was deoxygenated by CO<sub>2</sub>- and O<sub>2</sub>-free argon. Copper(II) chloride stock solution was prepared before use from CuCl<sub>2</sub>·xH<sub>2</sub>O in  $1.0 \times 10^{-2}$  M HCl and standardized by ICP-AES. HCl solution was titrated by standardized NaOH in a methanol/water solution. Carbonate-free NaOH solution was standardized by titration with potassium hydrogen phthalate.

The potentiometric titrations were performed using an automatic titrator system Titrando 905 (Metrohm) with a combined glass electrode (Mettler Toledo InLab Semi-Micro) filled with 0.1 M NaCl in a MeOH/H<sub>2</sub>O (80:20 w/w) mixture. The ionic strength was fixed at  $I = 0.1$  M with NaCl. The electrode was calibrated daily in hydrogen ion concentration using HCl.<sup>17</sup> The cell was thermostatted at  $25.0 \pm 0.2$  °C. A stream of argon, presaturated with methanol/water vapor, was passed over the surface of the solution. The ionic product of water for these conditions was  $10^{-14.42} \text{ mol}^2 \text{ dm}^{-6}$ . All the titrations were carried out on 3 mL samples. Metal–ligand system titrations were performed on solutions of **HPicHA** concentrations of  $2\text{--}3 \times 10^{-3}$  M and copper(II)-to-**HPicHA** molar ratios of 1:2 and 1:3.

The potentiometric data (about 140 points collected over the pH range 2–11) were refined with the Superquad<sup>18</sup> or Hyperquad 2000<sup>19</sup> programs, which use nonlinear least-squares methods.<sup>18–20</sup> Potentiometric data points were weighted by a formula allowing greater pH errors in the region of an end-point than elsewhere. The weighting factor  $W_i$  is defined as the reciprocal of the estimated variance of measurements:

$$W_i = 1/\sigma_i^2 = 1/[\delta_E^2 + (\delta E/\delta V)^2 \delta_V^2] \quad (1)$$

where  $\delta_E^2$  and  $\delta_V^2$  are the estimated variances of the potential and volume readings, respectively. The constants were refined by minimizing the error-square sum,  $U$ , of the potentials:

$$U = \sum_i^N W_i (E_{\text{obs},i} - E_{\text{cal},i})^2 \quad (2)$$

The quality of fit was judged by the values of the sample standard deviation,  $S$ , and the goodness of fit,  $\chi^2$  (Pearson's test). At  $\sigma_E = 0.1$  mV ( $0.0023 \sigma_{\text{pH}}$ ) and  $\sigma_V = 0.003$  mL, the value of  $S$  was 0.34, and  $\chi^2$  was below 12.6. The scatter of residuals versus pH was reasonably random, without any significant systematic trends, thus indicating a good fit of the experimental data.

The successive protonation constants were calculated from the cumulative constants determined with the program. The uncertainties in the log  $K$  values correspond to the added standard deviations in the cumulative constants. The distribution curves of the protonated species of L as a function of pH were calculated using Hyss 2006 program.<sup>21</sup>

pH-dependent UV–visible titrations were performed in two series of experiments: one in the pH range of 1–2 and the second between pH 2 and 11. In the first series, the stock solution of copper complexes was divided into various batches, with a constant total volume of 1.5 mL. In a pH range from 1 to 2, the pH was controlled by the concentration of the chloride acid. Ionic strength was adjusted to 0.1 M with the addition of NaCl. After preparation, each solution was allowed to equilibrate for 50–60 min, and then its visible spectrum was recorded. Absorption spectra were recorded using a Varian CARY 300 UV/vis spectrophotometer.

In the second set of experiments, 15 mL of solution containing a 1:3 molar ratio of Cu(II)/ligand where copper concentration was around  $1 \times 10^{-3}$  M was introduced into a jacketed cell (Metrohm) maintained at  $25.0 \pm 0.2$  °C. The initial pH was adjusted to around 2 with HCl, and the titration of the complex ( $2 < \text{pH} < 11$ ) was then carried out by the addition of known volumes of  $\sim 0.1$  M sodium hydroxide by the Titrand 905 (Metrohm) titrator (*vide infra*). Simultaneous pH and UV–visible measurements (200–900 nm) were recorded. Absorption spectra were recorded using a Varian CARY 50 UV/vis spectrophotometer fitted with Hellma optical fibers and an immersion probe. Data were analyzed using the SPECFIT/32 software.<sup>22</sup> Corrections were made for dilution due to the addition of base. Uncertainties in log  $\beta$  and the protonation constants were calculated from the standard deviation.

**Synthesis of Coordination Compounds. Caution!** Although no problems were encountered in this work, transition metal perchlorate complexes are potentially explosive and should be handled with proper precautions.

$[\text{Cu}_3(\text{PicHA-H})_2(\text{dipy})_2](\text{ClO}_4)_2 \cdot 4/3\text{DMSO} \cdot 2/3\text{H}_2\text{O}$  (1). An aqueous solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.1 M, 3 mL, 0.3 mmol) was added to a solution of HPicHA in methanol (0.1 M, 1 mL, 0.1 mmol) followed by 3 mL of methanol and a solution of dipy in DMSO (0.1 M, 2 mL, 0.2 mmol). The clear green solution was set aside for crystallization in a vacuum desiccator (over  $\text{CaCl}_2$ ). The resulting green fine crystals were filtered, washed with cold water, and air-dried. The crystals suitable for X-ray analysis were obtained by the slow vapor diffusion of iso-propanol to the solution of the complex, dissolved in DMSO (5 mL) at room temperature for four days. Yield: 70%. Calcd for  $\text{Cu}_3\text{C}_{34.67}\text{H}_{33.33}\text{N}_8\text{O}_{14}\text{Cl}_2\text{S}_{1.33}$  (1090.32): C, 38.19; H, 3.08; N, 10.28; Cu, 17.48%. Found: C, 37.96; H, 3.16; N, 10.45; Cu, 17.32%. ESI-MS (in methanol),  $m/z$  (%): 387.5 (100)  $[\text{Cu}_3(\text{PicHA-2H})_2(\text{dipy})_2]^{2+}$ ; 874.0 (12)  $\{[\text{Cu}_3(\text{PicHA-2H})_2(\text{dipy})_2]^{2+} + (\text{ClO}_4)^-\}^+$ .

$\text{Cu}(\text{PyDHA}) \cdot 2\text{H}_2\text{O}$  (2).  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.170 g, 1 mmol) was dissolved in 10 mL of water and added to a hot aqueous solution (15 mL) of  $\text{H}_2\text{PyDHA}$  (0.197 g, 1 mmol). The resulting dark green solution was set aside for evaporation in the air at room temperature. A fine crystalline precipitate was formed after 48 h, which was filtered off, washed with water, and air-dried. Yield: 71%. Calcd for  $\text{Cu}_7\text{H}_9\text{N}_3\text{O}_6$  (294.71): C, 28.53; H, 3.08; N, 14.26; Cu, 21.56%. Found: C, 28.75; H, 3.14; N, 14.01; Cu, 21.59%.

$[\text{PPh}_4]\text{Cu}(\text{PyDHA-2H}) \cdot 4\text{H}_2\text{O}$  (3).  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.242 g, 1 mmol) was dissolved in 10 mL of water and added to an aqueous solution (15 mL) of  $\text{H}_2\text{PyDHA}$  (0.197 g, 1 mmol). To the obtained suspension was added gradually 4 mL of a 1 M aqueous solution of sodium hydroxide, followed by 10 mL of a 0.2 M solution of tetraphenylphosphonium bromide in methanol. After 24 h, a dark green fine crystalline precipitate was filtered off, washed with water, and air-dried. Yield: 81%. Calcd for  $\text{CuC}_{55}\text{H}_{51}\text{N}_3\text{O}_8\text{P}_2$  (1007.52): C, 65.57; H, 5.10; N, 4.17; Cu, 6.31%. Found: C, 65.22; H, 5.31; N 4.33; Cu 6.58%.

$[\text{Cu}_2(\text{PyDHA})(\text{dipy})_2(\text{ClO}_4)_2] \cdot \text{DMF} \cdot \text{H}_2\text{O}$  (4). An aqueous solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.1 M, 2 mL, 0.2 mmol) was added to a solution of  $\text{H}_2\text{PyDHA}$  in water (0.1 M, 1 mL, 0.1 mmol) followed by a solution of dipy in methanol (0.1 M, 2 mL, 0.2 mmol). The resulting clear green solution was cooled to 5 °C, producing a fine crystalline precipitate, which was filtered off, washed with cold water, air-dried, and redissolved in DMF (3 mL) followed by filtration. The crystals, suitable for X-ray analysis were obtained from the filtrate by slow vapor diffusion of diethyl ether for two days. Yield: 77%. Calcd for  $\text{Cu}_2\text{C}_{30}\text{H}_{30}\text{N}_8\text{O}_{14}\text{Cl}_2$  (924.61): C, 38.97; H, 3.27; N, 12.12; Cu, 13.75%. Found: C, 38.89; H, 3.21; N, 12.24; Cu, 13.79%. ESI-MS (in methanol),  $m/z$  (%): 632.0 (100)  $\{[\text{Cu}_2(\text{PyDHA})_2(\text{dipy})_2]^{2+} - \text{H}^+\}^+$ .

$[\text{Cu}_3(\text{PyDHA-2H})(\text{tmeda})_3](\text{ClO}_4)_2$  (5). An aqueous solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.1 M, 3 mL, 0.3 mmol) was added to a solution of  $\text{H}_2\text{PyDHA}$  in water (0.1 M, 1 mL, 0.1 mmol) followed by an aqueous solution of tmeda (1 M, 0.3 mL, 0.3 mmol). The resulting solution was set aside for crystallization by slow evaporation at room temperature for 2–3 days. The resulting dark green crystals were filtered off, washed with cold water, and air-dried. Yield: 87%. Calcd for  $\text{Cu}_3\text{C}_{25}\text{H}_{51}\text{N}_9\text{O}_{12}\text{Cl}_2$  (931.28): C, 32.24; H, 5.52; N, 13.54; Cu, 20.47%. Found: C, 32.02; H, 5.70; N, 13.32; Cu, 20.58%. ESI-MS (in methanol),  $m/z$  (%): 366.1 (100)  $[\text{Cu}_3(\text{PyDHA-2H})(\text{tmeda})_3]^{2+}$ ; 308.0 (80)  $[\text{Cu}_3(\text{PyDHA-2H})(\text{tmeda})_2]^{2+}$ .

$\text{Cu}_3(\text{PyDHA-2H})(\text{dipy})_3(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (6). An aqueous solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.1 M, 1 mL, 0.1 mmol) was added to a solution of  $\text{H}_2\text{PyDHA}$  in water (0.1 M, 1 mL, 0.1 mmol), followed by an aqueous solution of sodium hydroxide (1 M, 0.2 mL, 0.2 mmol). Separately, an aqueous solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.1 M, 2 mL, 0.2 mmol) was mixed with a solution of dipy in methanol (0.1 M, 2 mL, 0.2 mmol) and with 5 mL of water. Both solutions were mixed, and an aqueous solution of sodium hydroxide (1 M, 0.2 mL, 0.2 mmol) and an aqueous solution of sodium perchlorate (1 M, 5 mL) were added sequentially to the obtained transparent green solution, producing a crystalline green precipitate, which was filtered off, washed with cold water, and air-dried. Yield: 83%. Calcd for  $\text{Cu}_3\text{C}_{37}\text{H}_{39}\text{N}_9\text{O}_{18}\text{Cl}_2$  (1159.31): C, 38.33; H, 3.39; N, 10.87; Cu, 16.44%. Found: C, 38.26; H, 3.18; N, 10.87; Cu, 16.30%. ESI-MS (in methanol),  $m/z$  (%): 426.0 (100)  $[\text{Cu}_3(\text{PyDHA-2H})(\text{dipy})_3]^{2+}$ ; 951.0 (5)  $\{[\text{Cu}_3(\text{PyDHA-2H})(\text{dipy})_3]^{2+} + (\text{ClO}_4)^-\}^+$ .

**X-Ray Crystallography.** Crystallographic and experimental details of crystal structure determinations are given in Table 4. X-ray data were collected on a Nonius Kappa CCD diffractometer at 120 K with a horizontally mounted graphite crystal as a monochromator and  $\text{Mo K}\alpha$  radiation. Data were collected and processed using *Denzo-Scalepack*<sup>23</sup> or *Collect*.<sup>24</sup> A semiempirical absorption correction (*SADABS*)<sup>25</sup> was applied to all data. The structures were solved by direct methods (*SHELXS-97*)<sup>26</sup> and refined by full-matrix least-squares on all  $F_o^2$  (*SHELXL-97*)<sup>27</sup> anisotropically for all non-hydrogen atoms. For structure representation, *ORTEP-3 for Windows* was used.<sup>28</sup>

1: The oxygen atoms in one of the perchlorate anions were disordered over two sites with occupancies 0.57/0.43. The Cl–O distances were restrained to be equal, and the anisotropic displacement

parameters of the disordered O atoms were restrained to be similar. The H<sub>2</sub>O H atoms were located from the difference Fourier map but constrained to ride on their parent atom, with  $U_{\text{iso}} = 1.5U_{\text{eq}}$  (parent atom). Other H atoms were positioned geometrically and were also constrained to ride on their parent atoms, with C–H = 0.95–0.98 Å and  $U_{\text{iso}} = (1.2–1.5)U_{\text{eq}}$  (parent atom).

4: The DMF solvent molecule was disordered with equal occupancies over two sites around a 2-fold axis sharing C15, C17, and O9. In the disordered DMF the distances C15–C17, C17–C18, and C18–C15 were restrained to be similar. Also, the solvent water was disordered around the inversion center with occupancies of 0.495/0.505. The hydrogen atoms of both disordered solvent molecules were omitted. Other hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C–H = 0.95 Å, N–H = 0.88 Å, and  $U_{\text{iso}} = 1.2U_{\text{eq}}$  (parent atom).

5: The carbon atoms C16 and C17 were disordered over two sites with occupancies 0.52/0.48. The methyl carbon atoms C14 and C19 were also disordered over two sites with occupancies 0.55/0.45 and 0.52/0.48, respectively. Furthermore, the oxygen atoms O6 and O8 were disordered over two sites with occupancies of 0.56/0.44. H atoms were positioned geometrically and were constrained to ride on their parent atoms, with C–H = 0.98–0.99 Å and  $U_{\text{iso}} = 1.2–1.5 U_{\text{eq}}$  (parent atom).


## RESULTS AND DISCUSSION

### Protonation and Complex Formation Equilibria.

Although the HPicHA ligand, HL, is soluble in water, its copper complexes were precipitating in water solution. Therefore in order to assess the potential speciation in the reaction system and identify the nature of the copper(II) species, experiments in a methanol/water mixture (80/20 w/w) have been performed.

To evaluate the coordination properties of the studied HPicHA ligand toward copper ions, first its acido–basic properties were determined. In the measured pH range, picolinehydroxamic acid indicates two protonation constants (Table 1). The first constant corresponds to proton

**Table 1.** Dissociation Constants of Pyridylhydroxamic Acids<sup>a</sup>



	HPicHA		H <sub>2</sub> PyDHA
	MeOH/H <sub>2</sub> O 80/20 w/w	H <sub>2</sub> O	H <sub>2</sub> O
pK <sub>a1</sub>	2.07(3)	1.85(4)	7.64
pK <sub>a2</sub>	9.64(1)	8.29(1)	8.80

<sup>a</sup>25 °C, 0.1 M NaClO<sub>4</sub>.

dissociation from the pyridine nitrogen atom, and the second, ionization of the hydroxamate group. While use of the mixed solvent did not affect very much the first dissociation constant, with only a 0.2 pK difference between water and the methanol/water system (Table 1), it was much more pronounced on the value of hydroxamic acid dissociation,  $pK_{a2(\text{MeOH/water})} = 9.64$  versus  $pK_{a2(\text{water})} = 8.29$ . However, such an increase of the hydroxamate dissociation constant in a methanol/water mixture is rather typical and has been already observed for  $\alpha$ -aminohydroxamate compounds<sup>29</sup> and hydroxamate artificial siderophores.<sup>30</sup> The proton dissociation equilibria for the H<sub>2</sub>PyDHA ligand, studied by us on a previous occasion, showed only two dissociation steps in aqueous solution (pH

range 2–11) corresponding to the ionization of two hydroxamic units (Table 1).<sup>12</sup> The dissociation of the pyridinium proton occurs obviously at a pH well below 2. Low values of protonation constants of pyridine nitrogen atoms in the case of HPicHA and H<sub>2</sub>PyDHA may contribute to the formation of its intramolecular hydrogen bonds with N–H or O–H groups of hydroxamic arms. Obviously, in the case of H<sub>2</sub>PyDHA, the protonation of the pyridine nitrogen atom is influenced by an inductive effect of two hydroxamic groups and the possibility of formation of bifurcate hydrogen bonds.

The  $pK_{\text{NHOH}}$  values for studied pyridylhydroxamic acids are more than 1 order of magnitude lower than typical values characteristic for aliphatic hydroxamic acids, and at least 0.5 log units lower than for aromatic hydroxamic acids.<sup>31</sup> This clearly indicates the noticeable electron accepting effect of the pyridine rings, which leads to depletion of the electron density of the hydroxamic groups and facilitates the dissociation of O–H protons. The dissociation constant corresponding to the ionization of the first hydroxamate group of H<sub>2</sub>PyDHA is 0.65 log units lower than for HPicHA, and this effect may be associated with an inductive effect of the second hydroxamic group.

Before describing the interactions between the HPicHA ligand and Cu(II), it has to be underlined that the total complexation of the Cu(II) ion with this ligand is essentially complete at pH 2. Therefore, complex formation constants could not be determined directly from potentiometric titration, and the use of a UV–vis and potentiometric data combination was necessary. First, the stability constant of the first formed species,  $\log K_{\text{CuL}} = 12.6(2)$ , was determined from the spectrophotometric pH-dependent batch titration, carried out in a pH range of 1–2 (Figure S1). This value was further used as a constant value in the potentiometric or spectrophotometric titrations carried out in a pH range from 2 to 11. Overall, the speciation model obtained shows the formation of four complexes:  $[\text{CuL}]^+$ ,  $[\text{Cu}_5(\text{LH}_{-1})_4]^{2+}$ ,  $[\text{CuL}_2]$ , and  $[\text{CuL}_2\text{H}_{-1}]^-$  (Table 2, Figure 1). The negative number of protons in the notation of complexes means deprotonation and possible participation in the metal binding of protons not dissociable during ligand titration performed over a pH range of 2 to 11. It is equivalent to the (PicHA-H) and (PyDHA-2H) notation used mainly in the description of isolated complexes.

A UV–vis absorption d–d band, present in the pH range 1–2, centered at 735 nm with  $\epsilon$  of 70 M<sup>-1</sup> cm<sup>-1</sup> and high stability of the first species (Table 2) indicate that copper(II) coordination may be realized through two nitrogen donor atoms. Just above pH 2, a new d–d band appears, with a maximum at 575 nm ( $\epsilon = 450 \text{ M}^{-1} \text{ cm}^{-1}$ ), confirming the formation of 12-metallacrown-4  $[\text{Cu}_5(\text{LH}_{-1})_4]^{2+}$  species (Scheme 3). Finally, above pH 8, the UV–vis spectral characteristics move further toward higher energies (Table 2, Figure S1) indicating four-N metal binding in  $[\text{CuL}_2]$  and  $[\text{CuL}_2\text{H}_{-1}]^-$  complexes.

Parameters of EPR spectra recorded in a solution at pH 1.5 also support the {N,N} binding mode for the  $[\text{CuL}]^+$  complex (Table 2, Figure S2). The complex dominating in the solution above this pH, e.g.  $[\text{Cu}_5(\text{LH}_{-1})_4]^{2+}$ , does not show an EPR spectrum, which is in agreement with the EPR behavior expected for such a type of polynuclear. The EPR spectrum reappears above pH 5, indicating the formation of mononuclear  $[\text{CuL}_2]$  and  $[\text{CuL}_2\text{H}_{-1}]^-$  species (Table 2, Figure S2).

In order to gain further evidence of the speciation model proposed for the Cu(II)–HPicHA system, ESI-MS experi-

Table 2. Complex Formation Constants and Spectroscopic Parameters of Cu(II) Complexes with HPicHA in Solution<sup>a</sup>

species	potentiometry		UV-vis		EPR	
	log $\beta$	log $\beta$	$\lambda_{\max}$ (nm)	$\epsilon$ (M <sup>-1</sup> cm <sup>-1</sup> )	$A_{II}(G)$	$g_{II}$
[CuL] <sup>+</sup>		12.6(2)	735	70	160	2.27
[Cu <sub>5</sub> (LH <sub>-1</sub> ) <sub>4</sub> ] <sup>2+</sup>	56.6(1)	56.04(7)	575	450	<i>b</i>	<i>b</i>
[CuL <sub>2</sub> ]	20.61(4)	20.21(9)	355	1.2 × 10 <sup>4</sup>		
			525	190	196	2.22
			355	2.75 × 10 <sup>3</sup>		
[CuL <sub>2</sub> H <sub>-1</sub> ] <sup>-</sup>	10.98(3)	10.7(1)	540	135	196	2.22
			355	2.75 × 10 <sup>3</sup>		

<sup>a</sup>Solvent: MeOH/H<sub>2</sub>O 80:20 w/w, *I* = 0.1 M (NaCl), *T* = (25.0 ± 0.2) °C. The reported errors on log  $\beta$  are given as 1 $\sigma$  and experimental errors on  $\lambda_{\max}$  = ±2 nm. <sup>b</sup>EPR silent.

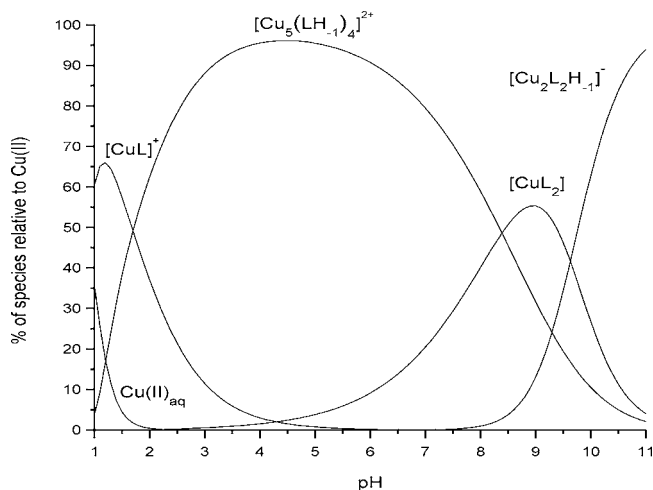
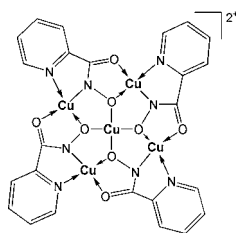


Figure 1. Species distribution diagram for the Cu(II)–HPicHA system in a metal-to-ligand molar ratio of 1:3. [L] = 3 × 10<sup>-3</sup> M.

### Scheme 3. Schematic Representation of the 12-MC-4 [Cu<sub>5</sub>(LH<sub>-1</sub>)<sub>4</sub>]<sup>2+</sup> Species



ments were carried out. Although the experiments with 1:1, 1:2, and 4:1 metal-to-ligand molar ratios were performed, mainly the 12-metallacrown-4 5:4 species ([Cu<sub>5</sub>(PicHA-H)<sub>4</sub>]<sup>2+</sup>, *m/z* = 430.4; [Cu(I)Cu(II)<sub>5</sub>(PicHA-H)<sub>4</sub>]<sup>+</sup>, *m/z* = 860.8; {[Cu<sub>5</sub>(PicHA-H)<sub>4</sub>]<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>)<sub>2</sub>]<sup>2+</sup>, *m/z* = 922.8; [Cu<sub>5</sub>(PicHA-H)<sub>4</sub>]<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>)<sub>3</sub>]<sup>-</sup>, *m/z* = 1046.7) and 15-metallacrown-5 5:5 complexes formed by trace metal cations like Ca(II) ((Ca<sup>2+</sup>)-[Cu<sub>5</sub>(PicHA-H)<sub>5</sub>]<sup>2+</sup>, *m/z* = 518.4; {(Ca<sup>2+</sup>)[Cu<sub>5</sub>(PicHA-H)<sub>5</sub>-(NO<sub>3</sub><sup>-</sup>)<sub>2</sub>]<sup>2+</sup>, *m/z* = 1098.7) or Na(I) ((Na<sup>+</sup>)[Cu<sub>5</sub>(PicHA-H)<sub>5</sub>]<sup>+</sup>, *m/z* = 1019.8) (Figure S3) could be detected. The presence of the mononuclear {[Cu(PicHA-H)<sub>2</sub>](H<sup>+</sup>)<sup>+</sup> (*m/z* = 338.0) complex was also confirmed. The experimental isotopic patterns of the complexes were in perfect agreement with simulated isotopic distributions.

As shown in Table 2 and Figure 1, the 12-MC-4 species is very stable and predominates over pH range 2–8. The log  $\beta$  of 56.6(1) is the highest determined up to now for the 12-MC-4

species;<sup>2e</sup> however, one has to remember that the current thermodynamic data have been obtained in a methanol/water mixture (80:20 w/w). A high amount of methanol in solvent composition, e.g. methanol/water 9:1 v/v, was shown to increase the log  $\beta$  of 12-MC-4 of (*S*)-phenylalaninehydroxamic acid, Pheha, and (*S*)-tryptophanhydroxamic acid, Trpha, *ca.* 8–11 orders of magnitude in comparison to other  $\alpha$ -amino-hydroxamates in water.<sup>2e,29</sup> Still the stability of the current 12-metallacrown-4 complex of HPicHA is around 4 orders of magnitude higher than analogous species of Pheha or Trpha.<sup>29</sup> Therefore, it can be concluded that the stabilization of the metallacrown complex comes from the intrinsic property of the ligand and complex structures, supported by subtle effects of organic solvent, like specific solvation effects, or electric permeability.

In our earlier paper, it was demonstrated that with an excess of the ligand, copper(II) forms with H<sub>2</sub>PyDHA a series of 1:1 complexes with different degrees of the ligand's deprotonation.<sup>12</sup> Here, in order to gain additional information on the speciation model obtained by potentiometry, ESI mass spectrometry control experiments on Cu(II)–H<sub>2</sub>PyDHA solutions have been performed, both in positive- and negative-ion modes. The reaction of copper(II) ions with H<sub>2</sub>PyDHA in a 1:1 metal-to-ligand ratio (in MeOH/H<sub>2</sub>O 80:20 w/w, at pH 3) revealed quite complicated processes of complex formation, with signals indicating mono-, bi-, tri-, and even tetra- or pentanuclear species, mostly with the metal-to-ligand stoichiometry of 1:1. In particular, intensive ESI-MS signals corresponding to the following species were observed: {[Cu(PyDHA)<sub>2</sub>]<sup>2-</sup>(H<sup>+</sup>)<sub>3</sub>]<sup>+</sup>, *m/z* = 456.0; [Cu<sub>2</sub>(PyDHA)<sub>2</sub>-(H<sup>+</sup>)<sup>+</sup>]<sup>+</sup>, *m/z* = 516.9; {[Cu<sub>2</sub>(PyDHA)<sub>2</sub>]- (H<sup>+</sup>)<sup>-</sup>]<sup>-</sup>, *m/z* = 514.9; [Cu<sub>2</sub>(PyDHA)<sub>2</sub>](Na<sup>+</sup>)<sup>+</sup>, *m/z* = 538.9; {[Cu<sub>3</sub>(PyDHA)<sub>3</sub>](H<sup>+</sup>)<sup>+</sup>]<sup>+</sup>, *m/z* = 776.9; {[Cu<sub>3</sub>(PyDHA)<sub>3</sub>]- (H<sup>+</sup>)<sup>-</sup>]<sup>-</sup>, *m/z* = 774.9; {[Cu<sub>3</sub>(PyDHA)<sub>3</sub>](Na<sup>+</sup>)<sup>+</sup>]<sup>+</sup>, *m/z* = 798.9; {[Cu<sub>4</sub>(PyDHA)<sub>4</sub>]- (H<sup>+</sup>)<sup>-</sup>]<sup>-</sup>, *m/z* = 1032.8; and {[Cu<sub>5</sub>(PyDHA)<sub>5</sub>]- (H<sup>+</sup>)<sup>-</sup>]<sup>-</sup>, *m/z* = 1290.7 (Figure S4). In positive-ion mode, one can additionally identify a variety of signals of multinuclear copper patterns, corresponding to species with a nuclearity up to 10, e.g., {[Cu<sub>4</sub>(PyDHA)<sub>4</sub>-(Cu<sup>2+</sup>)<sup>2+</sup>]<sup>2+</sup>, *m/z* = 548.4; {[Cu<sub>4</sub>(PyDHA)<sub>4</sub>](Cu<sup>2+</sup>)<sub>2</sub>-2(H<sup>+</sup>)<sup>2+</sup>]<sup>2+</sup>, *m/z* = 579.8, {[Cu<sub>5</sub>(PyDHA)<sub>5</sub>](Cu<sup>2+</sup>)<sub>2</sub>-2(H<sup>+</sup>)<sup>2+</sup>]<sup>2+</sup>, *m/z* = 708.8; {[Cu<sub>6</sub>(PyDHA)<sub>6</sub>](Cu<sup>2+</sup>)<sub>2</sub>-2(H<sup>+</sup>)<sup>2+</sup>]<sup>2+</sup>, *m/z* = 837.8; {[Cu<sub>7</sub>(PyDHA)<sub>5</sub>(PyDHA-2H)<sub>2</sub>](Cu<sup>2+</sup>)<sub>3</sub>]<sup>2+</sup>, *m/z* = 998.2; or {[Cu<sub>4</sub>(PyDHA)<sub>4</sub>](Cu<sup>2+</sup>)- (H<sup>+</sup>)<sup>+</sup>]<sup>+</sup>, *m/z* = 1095.8 (Figure S4).

An excess of copper(II) in the reaction mixture gave identical spectra. Since in the majority of the observed species the metal-to-ligand molar ratio is 1:1, they could not be distinguished by

Table 3. IR, UV–Vis, and EPR Spectroscopic Data of the Solid-State Complexes

compound	IR, $\nu$ , $\text{cm}^{-1}$				UV–vis, $\nu$ , nm			EPR (powder)
	$\nu_{\text{N-O}}$ hydroxamate	$\nu_{\text{Cl-O}}$ perchlorate	$\nu_{\text{C=O}}$ amide I	$\nu_{\text{O-H}}$	electronic absorption ( $\epsilon$ , $\text{M}^{-1} \text{cm}^{-1}$ )	diffuse reflection		
HPicHA	910, 1026		1651	3341				
H <sub>2</sub> PyDHA	887, 1026		1643	3279				
[Cu <sub>3</sub> (PicHA-H) <sub>2</sub> (dipy) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·4/3 DMSO·2/3H <sub>2</sub> O (1)	923, 1044	660, 1100	1590	3420	596 (120) sh	594	$g_{\text{iso}} = 2.099$ (2.087) <sup>a</sup>	
Cu(PyDHA)·2H <sub>2</sub> O (2)	923, 1034		1615	3220	640 (58)	638	$g_{\parallel} = 2.240$ (2.244), <sup>a</sup> $g_{\perp} = 2.077$ (2.079) <sup>a</sup>	
[PPh <sub>4</sub> ] <sub>2</sub> Cu(PyDHA-2H)·4H <sub>2</sub> O (3)	920, 1041		1610	3320	558 (77)	559	$g_{\parallel} = 2.252$ (2.256), <sup>a</sup> $g_{\perp} = 2.085$ (2.085) <sup>a</sup>	
[Cu <sub>2</sub> (PyDHA)(dipy) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ] DMF·H <sub>2</sub> O (4)	935, 1051	650, 1100	1605	3435	658 (63)	632	$g_{\text{iso}} = 2.104$ (2.099) <sup>a</sup>	
[Cu <sub>3</sub> (PyDHA-2H)(tmeda) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub> (5)	925, 1036	655, 1100	1600	3435	623 (39)	625	$g_{\text{iso}} = 2.095$ (2.071) <sup>a</sup>	
Cu <sub>3</sub> (PyDHA-2H)(dipy) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O (6)	922, 1035sh	655, 1090	1610	3150	617 (43)	625	$g_{\text{iso}} = 2.111$ (2.098) <sup>a</sup>	

<sup>a</sup>At 78 K; sh, shoulder.

pH-potentiometric titrations, which is in full accordance with our earlier observations.<sup>12</sup>

**Isolation and Characterization of Coordination Compounds.** Isolation of copper(II) complexes of HPicHA from water-containing solution is rather difficult, as the process may be complicated by ligand hydrolytic degradation to *o*-picolinic acid (*o*-Pica), which is known to be significantly accelerated with an increase of pH.<sup>32</sup> Clearly, this has been manifested in the stepwise change of the color of solutions from dark green to blue with consequent formation of bright blue crystals of earlier reported *catena*-[Cu(*o*-Pica-H)<sub>2</sub>]<sub>n</sub>·2nH<sub>2</sub>O.<sup>32</sup> It has been observed that the latter can be formed together with green crystals of hydroxamate-containing complexes.<sup>33</sup>

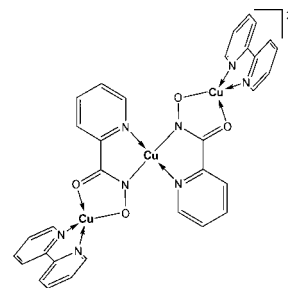
Although the 12-MC-4 species predominates the Cu(II)-HPicHA solution, we have launched attempts to prepare polynuclear complexes of non-MC topology. The addition of a strong chelating agent to the in situ formed pentanuclear 12-MC-4 copper(II) complex was used as an approach, as up to now, the behavior of metallacrowns in such a reaction mixture has not been studied in detail. Only Seda et al.<sup>10</sup> have demonstrated that even in the presence of nonchelating ligand pyridine, the PicHA-based 12-MC-4 copper(II) complex undergoes degradation, resulting in the formation of a trinuclear product.

The addition of 2 equiv of dipy to the reaction mixture containing copper(II) and HPicHA in a metal-to-ligand molar ratio of 3:1, followed by slow diffusion of iso-propanol vapors, resulted in the single crystals of the trinuclear compound [Cu<sub>3</sub>(PicHA-H)<sub>2</sub>(dipy)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·4/3DMSO·2/3H<sub>2</sub>O (1). Preliminary conclusions about the structure of 1 were made on the basis of satisfactory results of elemental analysis (*cf.* Experimental Section) and ESI mass spectra. The latter clearly shows a prominent peak envelope at an *m/z* of 387.5 with a characteristic isotopic pattern, which corresponds to the trinuclear complex cation [Cu<sub>3</sub>(PicHA-H)<sub>2</sub>(dipy)<sub>2</sub>]<sup>2+</sup> (*cf.* Experimental Section).

On the basis of the analysis of ESI mass spectra, IR, electronic, and EPR spectroscopic data (Table 3), it could be concluded that the obtained complex indicates the {(N,N'); (O,O')} bis(chelate)-bridging coordination mode of the hydroxamate ligands (Scheme 1), whereas the hetroarylamine ligands exhibit a typical (N,N')-chelate coordination pattern. Clearly, 1 contains two types of central atoms, e.g. surrounded by various donor groups. The presence of the broad

asymmetric bands in the range 593–660 nm in the electronic absorption spectrum and diffusion reflection spectrum may indicate the presence of two different chromophores, with maxima characteristic for mixed nitrogen–oxygen surroundings. Obviously, 1 has both CuN<sub>2</sub>O<sub>2</sub> and CuN<sub>4</sub> chromophores (Scheme 4). The positions of maxima in the diffusion

Scheme 4. Ligands Coordination in [Cu<sub>3</sub>(PicHA-H)<sub>2</sub>(dipy)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·4/3DMSO·2/3H<sub>2</sub>O (1)



reflectance spectra of the solid compound are practically unchanged compared with the electronic absorption spectra, indicating preservation of the coordination sphere in solution.

Although isolation of copper(II) complexes of H<sub>2</sub>PyDHA on the occasion of our previous paper<sup>12</sup> was unsuccessful, recently the addition of alkali to an aqueous solution of copper(II)–H<sub>2</sub>PyDHA in a 1:2 molar ratio resulted in an isolation of two compounds, Cu(PyDHA)·2H<sub>2</sub>O (2) and [PPh<sub>4</sub>]<sub>2</sub>Cu(PyDHA-2H)·4H<sub>2</sub>O (3). The latter was obtained by the addition of 4 equiv of NaOH, with subsequent substitution of sodium cations by tetraphenylphosphonium. Note that according to our previous pH-potentiometric results, the corresponding complex species were found in solution under appropriate pH, and their appearance was, as now, accompanied by a short-wave shift of the absorption maximum of d–d transitions.<sup>12</sup> The proposed coordination mode of H<sub>2</sub>PyDHA in 2 and 3 is presented in Scheme 2.

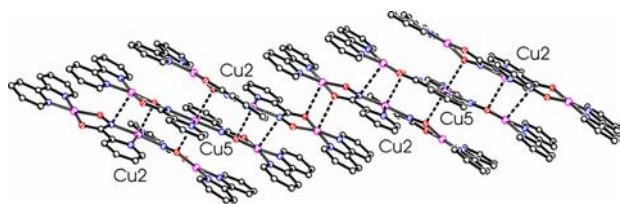
Following the results of ESI-MS experiments (*vide supra*), attempts to isolate or crystallize appropriate polynuclear complexes from the corresponding solutions were unsuccessful and did not lead to analytically pure products, which could be identified as individual compounds. This difficulty presumably comes from a very complex equilibrium occurring in the

system, involving various polynuclear species of different nuclearities, with none of them dominating. To overcome the problem, the use of bidentate chelating ligands able to saturate vacant positions in the coordination sphere of copper(II) ions was applied. Indeed, on the addition of dipy or tmeda to aqueous or methanolic solutions containing copper(II) and  $\text{H}_2\text{PyDHA}$  in metal-to-ligand molar ratios of 2:1 and 3:1, the bi- $[\text{Cu}_2(\text{PyDHA})(\text{dipy})_2(\text{ClO}_4)_2] \cdot \text{DMF} \cdot \text{H}_2\text{O}$  (**4**) and trinuclear  $[\text{Cu}_3(\text{PyDHA-2H})(\text{tmeda})_3](\text{ClO}_4)_2$  (**5**) and  $\text{Cu}_3(\text{PyDHA-2H})(\text{dipy})_3(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (**6**) complexes were obtained. ESI-MS of the three regarded complexes confirm the presence of bi- (**4**) and trinuclear (**5**, **6**) species in solution (*cf.* Experimental Section).

Although EPR spectra of all synthesized polynuclear compounds (Table 3) are not very informative, they do provide additional arguments to support the formation of bi- or trinuclear complexes. A broad isotropic signal observed in trinuclear complexes is obviously a result of antiferromagnetic exchange interaction between the central atoms (confirmed by magnetochemical studies, *vide infra*). At the same time, antiferromagnetic interaction in the trinuclear copper(II) compounds results in a spin doublet, observed in the EPR spectra.

IR spectra of all synthesized complexes (Table 3) demonstrated low frequency shifts of the amide I ( $\text{C}=\text{O}$ ) ( $\Delta\nu = 28\text{--}61 \text{ cm}^{-1}$ ) and high-frequency shifts of  $\nu(\text{N}-\text{O}_{\text{hydroxamate}})$  ( $\Delta\nu = 13\text{--}35$  and  $8\text{--}25 \text{ cm}^{-1}$ ) bands compared with their position in the spectra of **HPicHA** and **H<sub>2</sub>PyDHA** (Table 3). Such shifts are typical for N-coordinated deprotonated hydroxamate groups.<sup>2a,b,d</sup> Intensive absorption bands observed at  $625\text{--}660$  and  $1090\text{--}1100 \text{ cm}^{-1}$  correspond to  $\nu(\text{Cl}-\text{O})$  stretching of the perchlorate anions.

**X-Ray Structural Studies. Molecular Structure of  $[\text{Cu}_3(\text{PicHA-H})_2(\text{dipy})_2](\text{ClO}_4)_2 \cdot 4/3\text{DMSO} \cdot 2/3\text{H}_2\text{O}$  (**1**).** The structure is ionic and consists of the one-dimensional cationic polymeric chains composed of three-decked stacks of double-charged trinuclear complex cations  $[\text{Cu}_3(\text{PicHA-H})_2(\text{dipy})_2]^{2+}$ , perchlorate anions, and solvate molecules of DMSO and water (Figure 2, see also Table 4). The elements of the crystal



**Figure 2.** Organization of the complex cations in three-decked stacks and their further integration into a 1D chain in  $[\text{Cu}_3(\text{PicHA-H})_2(\text{dipy})_2](\text{ClO}_4)_2 \cdot 4/3\text{DMSO} \cdot 2/3\text{H}_2\text{O}$  (**1**). Axial contacts  $\text{Cu}-\text{O}$  and  $\text{Cu}-\text{N}$  are marked by dashed lines.

structure are united through the hydrogen bonds and van der Waals interactions. The unit cell contains two crystallographically independent conformers of the complex cation. One of them lies in a crystallographic inversion center (atom Cu (5)), whereas in the second one, the medial copper(II) ion, Cu(2), takes a common position. The crystallographically centrosymmetric complex cation is situated in the middle of the three-decked stacks, while crystallographically noncentrosymmetric complex cations lie on the top and bottom of the stacks. Two conformers differ slightly by their geometrical and

conformational parameters. The  $\text{Cu}\cdots\text{Cu}$  distances between the medial and the terminal ions are in the range of  $4.6198(7)\text{--}4.7136(5) \text{ \AA}$  (Figure 2).

The trinuclear complex cation consists of three copper(II) ions, two molecules of neutral dipy ligands, and two double-deprotonated residues of **HPicHA** (Figure 3). Dipy ligands are coordinated to two terminal copper(II) ions through a typical chelating mode. The hydroxamate ligands are coordinated by the  $\{(O,O')(N,N')\}$ -(bis)bidentate-bridging coordination mode, forming a bridge between the medial, Cu(2), and the terminal, Cu(1) and Cu(3), copper(II) ions, thus forming two adjacent chelate rings. Herewith, the medial Cu(2) atom is surrounded by pyridine and hydroxamate nitrogen donor atoms from two **HPicHA** ligands located in the trans position with respect to each other; the terminal copper(II) atoms are coordinated by the oxygen atoms of the hydroxamate anions.

The copper ions, located in the medial position of the complex (Cu(2) and Cu(5) for the first and the second conformer, respectively), are in a distorted octahedral or regular octahedral environment (as Cu(5) lies on the center of inversion). The equatorial planes of Cu(II) coordination spheres are occupied by four nitrogen atoms belonging to two hydroxamate ligands. The apical positions are taken by the oxygen atoms (O(5) and O(3), respectively, for Cu(2) and Cu(5)), from the N-O group of the hydroxamate functions of a neighboring conformer. The Cu-N bond lengths are in the range of  $1.951(3)\text{--}2.027(4) \text{ \AA}$ , with the Cu-N(Py) distances slightly longer than the Cu-N(hydroxamate) (Table 1). The axial contacts,  $\text{Cu}(2)\text{--O}(5) = 2.522(3)$  and  $\text{Cu}(5)\text{--O}(3) = 2.534(3) \text{ \AA}$ , are significantly longer than the equatorial Cu-N distances.

Also, all terminal copper(II) ions are in a distorted tetragonal-pyramidal environment ( $\tau = 0.11, 0.14,$  and  $0.07$  for Cu(1), Cu(3), and Cu(4), respectively).<sup>34</sup> Their equatorial coordination is formed by two nitrogen atoms of dipy ( $\text{Cu}-\text{N} = 1.961(4)\text{--}1.969(4) \text{ \AA}$ ) and two hydroxamate oxygen atoms ( $\text{Cu}-\text{O} = 1.898(3)\text{--}1.923(3) \text{ \AA}$ ). The axial positions are occupied by oxygen or nitrogen atoms of neighboring or translational complex cations, or perchlorate anions.

In the crystal packing, three neighboring trinuclear complex cations are organized into three-decked stacks due to the long axial Jahn-Teller contacts  $\text{Cu}(2)\text{--O}(5) = 2.523(3)$ ,  $\text{Cu}(5)\text{--O}(3) = 2.535(3)$ , and  $\text{Cu}(4)\text{--N}(4) = 2.936(4) \text{ \AA}$  (Figure 2). Further association of the stacks into a polymeric cationic column is realized by the axial contacts,  $\text{Cu}(1)\text{--O}(2) (-x - 1, -y, -z + 1) = 2.792(3) \text{ \AA}$ .

**Molecular Structure of  $[\text{Cu}_2(\text{PyDHA})(\text{dipy})_2](\text{ClO}_4)_2 \cdot \text{DMF} \cdot \text{H}_2\text{O}$  (**4**).** The structure is made up of the stair-like chains formed by neutral dinuclear complex species  $[\text{Cu}_2(\text{PyDHA})(\text{dipy})_2(\text{ClO}_4)_2]$  and solvate DMF and water molecules associated with the chains through the hydrogen bonds. Given the relatively small distance between the neighboring dinuclear species ( $\text{Cu}(1)\cdots\text{Cu}(1)^* = 3.3297(17) \text{ \AA}$ ), the compound can be considered a one-dimensional coordination polymer, formed by flat dinuclear complexes united through the Jahn-Teller axial  $\text{Cu}(1)\text{--O}(1) = 2.513(5) \text{ \AA}$  contacts in the stair-like chains located along  $z$  axis of the crystal (Figure 4).

The dinuclear complex (Figure 5) lies on the 2-fold axis, passing through the middle of the pyridine cycle; the N(4), C(14), and H(14) atoms; and the O(9), C(15), and C(17) atoms of the disordered DMF molecule. These atoms are characterized by an occupation factor of 0.5, so that each "half"

Table 4. Crystal Data and Structure Refinement for 1, 4, and 5

identification code	1	4	5
empirical formula	C <sub>104</sub> H <sub>100</sub> Cl <sub>6</sub> Cu <sub>9</sub> N <sub>24</sub> O <sub>42</sub> S <sub>4</sub>	C <sub>30</sub> H <sub>29</sub> Cl <sub>2</sub> Cu <sub>2</sub> N <sub>8</sub> O <sub>14</sub>	C <sub>25</sub> H <sub>51</sub> Cl <sub>2</sub> Cu <sub>3</sub> N <sub>9</sub> O <sub>12</sub>
fw	3270.88	923.59	931.27
cryst syst	triclinic	monoclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
unit cell dimensions	<i>a</i> = 14.288(4) Å <i>b</i> = 14.335(4) Å <i>c</i> = 16.676(3) Å $\alpha$ = 89.81(2)° $\beta$ = 67.12(2)° $\gamma$ = 76.96(2)°	16.950(1) 13.821(1) 17.921(1) $\beta$ = 107.71(4)	21.227(7) 7.795(3) 22.965(6) $\beta$ = 94.74(2)
volume	3052.10(13) Å <sup>3</sup>	3999.4(5)	3786.6(2)
Z	1	4	4
density (calcd)	1.780 Mg/m <sup>3</sup>	1.534 Mg/m <sup>3</sup>	1.634 Mg/m <sup>3</sup>
abs coeff	1.832 mm <sup>-1</sup>	1.269 mm <sup>-1</sup>	1.878 mm <sup>-1</sup>
F(000)	1655	1876	1924
cryst size	0.21 × 0.15 × 0.06 mm <sup>3</sup>	0.20 × 0.07 × 0.06 mm	0.26 × 0.25 × 0.07 mm
$\Theta$ range for data collection	2.92–27.00°	2.07–25.11°	2.73–25.00°
index ranges	–18 ≤ <i>h</i> ≤ 18, –18 ≤ <i>k</i> ≤ 18, –21 ≤ <i>l</i> ≤ 21	–20 ≤ <i>h</i> ≤ 20, –16 ≤ <i>k</i> ≤ 16, –19 ≤ <i>l</i> ≤ 21	–25 ≤ <i>h</i> ≤ 25, –9 ≤ <i>k</i> ≤ 9, –27 ≤ <i>l</i> ≤ 27
reflns collected	54289	12260	48076
independent reflns	13240 [R(int) = 0.0677]	3486 [R(int) = 0.0651]	6647 [R(int) = 0.0787]
completeness to $\Theta$ = 27.00°	99.4%	97.8%	99.7%
absorption correction	analytical	semiempirical	semiempirical
max. and min transmission	0.8980 and 0.7030	0.9323 and 0.7827	0.8798 and 0.6419
refinement method	full-matrix least-squares on F <sup>2</sup>	full-matrix least-squares on F <sup>2</sup>	full-matrix least-squares on F <sup>2</sup>
data/restraints/params	13240/64/895	3486/3/272	6647/24/508
goodness-of-fit on F <sup>2</sup>	1.026	1.063	1.048
final R indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	R1 = 0.0542, wR2 = 0.1314	R1 = 0.0797, wR2 = 0.2222	R1 = 0.0487, wR2 = 0.1158
R indices (all data)	R1 = 0.0884, wR2 = 0.1503	R1 = 0.1191, wR2 = 0.2491	R1 = 0.0745, wR2 = 0.1309
largest diff. peak and hole	2.174 and –1.029 e Å <sup>-3</sup>	1.312 and –0.701 e Å <sup>-3</sup>	1.182 and –1.396 e Å <sup>-3</sup>

of the complex (and thus, coordination sphere of each copper(II) ion) is crystallographically independent. The complex consists of two copper ions(II), two dipy chelating ligand molecules, one doubly deprotonated H<sub>2</sub>PyDHA residue, and two axially coordinated perchlorate ions. The hydroxamate ligand is coordinated through the classical bis-{(O,O'); (O'',O''')}-chelating mode bridging two copper(II) ions. Given the availability in H<sub>2</sub>PyDHA of a powerful tridentate donor set consisting of three nitrogen atoms,<sup>12</sup> the realization of the above-described coordination mode was somewhat unexpected. Very likely, the experimental approach, like a weak acidic medium of the reaction mixture, and usage of blocking dipy molecules prevented the realization of the tridentate binding mode. Indeed, a weak acidic medium of the reaction mixture is insufficient for the deprotonation of N–H hydroxamate functions, and the protection of two *cis*-positions in the coordination sphere of copper(II) ions by dipy molecules hampers the trinitrogen mode of binding. In addition, the realization of the *bis*-(O,O')-chelate coordination of H<sub>2</sub>PyDHA could be supported by the symmetry of the complex and the formation of symmetric bifurcate hydrogen bonds between the DMF molecule and hydroxamate NH protons, which effectively block the nitrogen donor atom of the pyridine cycle, locking it in a pseudomacrocyclic ring (Figure 4).

The copper(II) ion in the dinuclear complex is in a distorted octahedral environment. Two nitrogen and two oxygen atoms of dipy and H<sub>2</sub>PyDHA, respectively, provide equatorial coordination. The equatorial Cu–O distances are noticeably shorter than the Cu–N distances (Table S2). The axial

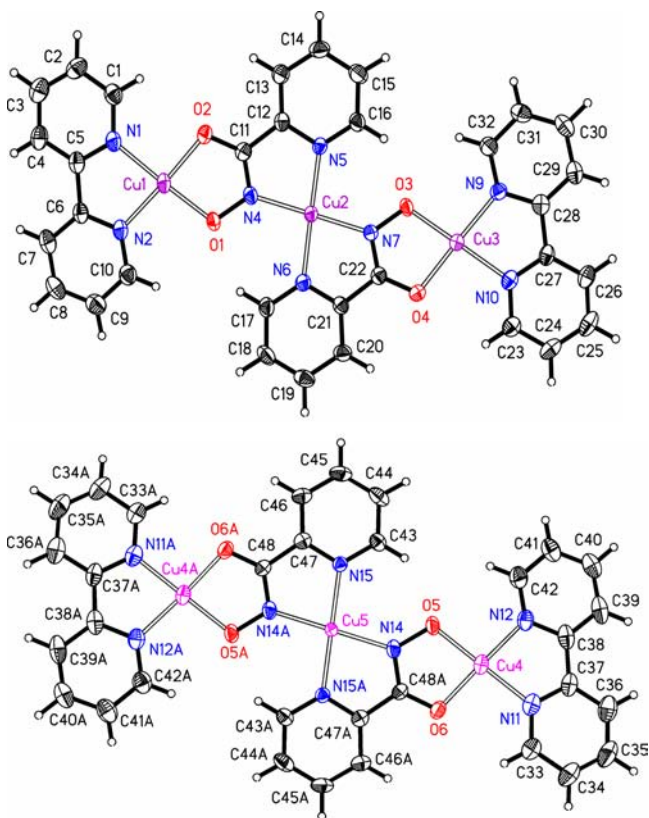
positions are occupied by the oxygen atom of the monodentately coordinated perchlorate ion (Cu(1)–O(5) = 2.737(8) Å) and the hydroxamate oxygen atom of the translational complex, related with the basic by the center of symmetry in the point (1 0 1) (Cu(1)–O(1)\* = 2.513(5) Å). As the lengths of the axial contacts are markedly different, the coordination number of the complex can be represented as 4 + 1 + 1. Obviously, these differences are associated with the Jahn–Teller effect and also with the partial charges on the oxygen atoms.

The Cu(1)···Cu(1)\*\* = 9.7496(18) separation between the copper atoms in the dinuclear fragment is much longer than the intermolecular Cu(1)···Cu(1)\* = 3.3297(17) distance between the adjacent dinuclear fragments organized in chains.

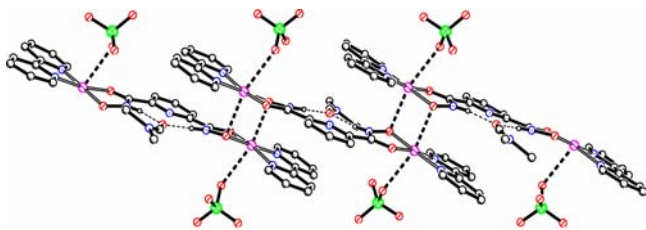
**Molecular Structure of [Cu<sub>3</sub>(PyDHA-2H)(tmeda)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> (5).** The structure is ionic and comprised of the double-charged complex cations [Cu<sub>3</sub>(PyDHA-2H)(tmeda)<sub>3</sub>]<sup>2+</sup> and perchlorate anions linked into the crystal only by van der Waals interactions. An absence of OH and NH protons, as well as solvate molecules of proton-donor solvents, prevents the formation of hydrogen bonds. Translational complex cations form columns, parallel to the *y* axis of the crystal, and the perchlorate ions occupy cavities between these columns.

The trinuclear complex cation (Figure 6) consists of three copper(II) ions, one 4-fold-deprotonated residue of H<sub>2</sub>PyDHA, and three amine tmeda ligands. Tmeda ligands are coordinated to all three copper(II) ions by a common bidentate mode with the formation of five-membered chelate rings. The hydroxamate ligand is coordinated by the {(O,O'); (N,N',N'')};

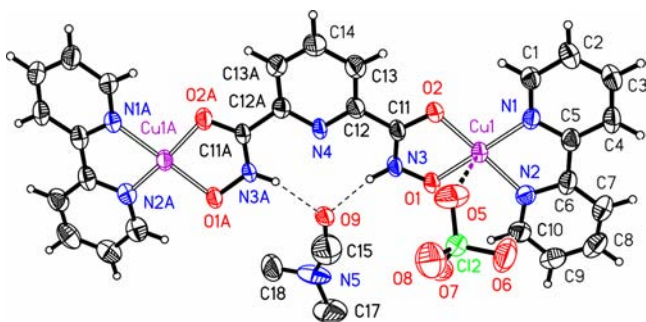




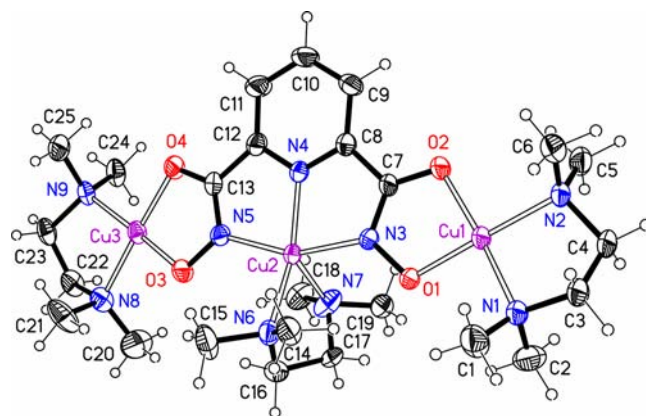
**Figure 3.** Molecular structure and numbering scheme for two conformers of the complex cation in  $[\text{Cu}_3(\text{PicHA-H})_2(\text{dipy})_2](\text{ClO}_4)_2 \cdot 4/3\text{DMSO} \cdot 2/3\text{H}_2\text{O}$  (1). Thermal ellipsoids are plotted at the 50% probability level. Symmetry codes: (A):  $-x, -y, -z$ .



**Figure 4.** Organization of the dinuclear subunits in a stair-like 1D polymer in the structure of  $[\text{Cu}_2(\text{PyDHA})(\text{dipy})_2](\text{ClO}_4)_2 \cdot \text{DMF} \cdot \text{H}_2\text{O}$  (4).



**Figure 5.** Molecular structure of  $[\text{Cu}_2(\text{PyDHA})(\text{dipy})_2](\text{ClO}_4)_2 \cdot \text{DMF} \cdot \text{H}_2\text{O}$  (4). The solvated water molecule, the second position of the disordered DMF, and the perchlorate ion coordinated to Cu(1A) are omitted for clarity. Thermal ellipsoids are plotted at the 50% probability level.



**Figure 6.** Structure of complex cation in  $[\text{Cu}_3(\text{PyDHA-2H})(\text{tmeda})_3](\text{ClO}_4)_2$  (5). Thermal ellipsoids are plotted at the 50% probability level.

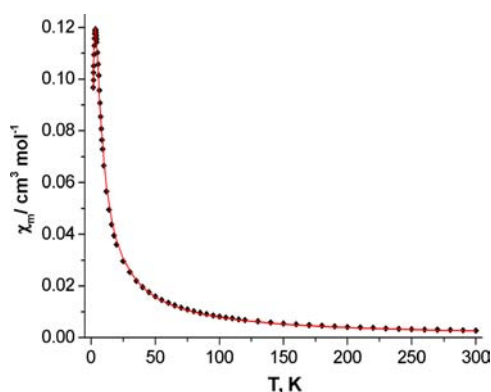
(O',O'')-tridentate-(bis)bidentate mode, bridging three copper(II) ions. The idealized molecular symmetry of the complex cation is close to  $C_{2v}$ , with a medial and two terminal copper ions(II); the latter similar with respect to their position in the molecule. However, because of significant linear and angular distortions, the real geometry of the complex is far from perfect.

The copper ion, which occupies the medial position in the complex (Cu(2)), is in a strongly distorted square-pyramidal environment ( $\tau = 0.01$ ) of five nitrogen atoms, three of which belong to the residue of  $\text{H}_2\text{PyDHA}$  and two to the bidentate tmeda ligand. The equatorial plane of the coordination sphere consists of the  $\text{H}_2\text{PyDHA}$  N(3), N(4), and N(5) and tmeda N(6) donor atoms. The apical position is occupied by the N(7) atom from the tmeda ligand. The axial contact,  $\text{Cu}(2)-\text{N}(7) = 2.212(5)$  Å, is significantly longer than the equatorial  $\text{Cu}-\text{N}$  distances, being in the range of  $1.946(4)-2.045(4)$  Å (Table S3). It is worthy to note a considerable difference between the  $\text{Cu}(2)-\text{N}(7)$  and  $\text{Cu}(2)-\text{N}(6)$  bond lengths (Table S3). Significant elongation of the  $\text{Cu}(2)-\text{N}(7)$  bond is evidently associated with the Jahn–Teller effect, and among five donor nitrogen atoms, the most acceptable choice is the bond between central atom and one of the tmeda donor atoms.

Due to a certain rigidity of the complex, imposed by the tridentate coordination of  $\text{H}_2\text{PyDHA}$ , a marked reduction of the interatomic  $\text{Cu}(2)-\text{N}(4)$  distance ( $1.946(4)$  Å) is observed. This is significantly shorter than typical  $\text{Cu}-\text{N}$  distances for the pyridine donors and relates to a specific position of the N(4) atom at the border of two adjacent chelate rings. On the contrary, the copper-hydroxamate nitrogen distances ( $\text{Cu}(2)-\text{N}(3)$  and  $\text{Cu}(2)-\text{N}(5)$ ) are atypically extended to  $2.019(4)$  and  $2.005(4)$  Å, respectively (Table S3). Usually, these distances are in the range of  $1.94-1.96$  Å. The coordination sphere of Cu(2) is also characterized by noticeable angular distortions (Table S3). In particular, the bite angles  $\text{N}(4)-\text{Cu}(2)-\text{N}(5)$  and  $\text{N}(4)-\text{Cu}(2)-\text{N}(3)$  of the two five-membered rings formed by  $\text{H}_2\text{PyDHA}$  are reduced to  $78.50(16)$  and  $78.74(16)$ , respectively, while the  $\text{N}(6)-\text{Cu}(2)-\text{N}(7)$  angle formed by a much more conformationally flexible ligand tmeda was only slightly less than  $90^\circ$  ( $86.78(19)^\circ$ ). It should be noted that the planes, defined by the atoms of the two adjacent five-membered chelates formed by  $\text{H}_2\text{PyDHA}$ , the central atom, and the N(6) and N(7) donor atoms, are almost perpendicular (the dihedral angle between

them is  $89.24(12)^\circ$ ). Each terminal Cu(1) and Cu(3) ion is in a distorted square-planar environment made up of two nitrogen atoms of the chelating tmeda ligand and two oxygen atoms of the chelating hydroxamate group of the  $\text{H}_2\text{PyDHA}$  ligand. The coordination spheres of both ions have noticeable linear distortions, caused by the presence of different types of donor atoms. The Cu–N distances are in the range of  $1.983(4)$ – $2.019(4)$  Å, which is typical for copper(II)–amine bond distances. There is a noticeable difference in the Cu–O bond lengths, formed by the central atom with the carbonyl ( $1.934(3)$  and  $1.948(4)$  Å) and the hydroxamate ( $1.892(3)$  and  $1.888(3)$  Å) oxygen atoms. The bite angles are reduced to  $84.79(14)$ – $87.80(17)$  (Table S3).

**Magnetochemical Studies.** The temperature dependence of magnetic susceptibility for solid samples of **1**, **4**, and **5** were collected in the temperature range 1.8–300 K. The dinuclear complex **4** shows, within a wide temperature range, a temperature independent magnetic moment ( $\chi T$  product is equal to  $0.845 \text{ cm}^3 \text{ K mol}^{-1}$  per two copper atoms) very close to the expected spin-only value for isolated copper(II) ions, which slightly drops on cooling below 150 K. Below 18 K, there is a rapid decrease of the  $\chi T$  product, which drops to  $0.174 \text{ cm}^3 \text{ K mol}^{-1}$  at 1.8 K (Figure 7). Obviously, such a behavior is a



**Figure 7.** Thermal dependence of  $\chi_m$  ( $\blacklozenge$ ) for compound  $[\text{Cu}_2(\text{PyDHA})(\text{dipy})_2(\text{ClO}_4)_2] \cdot \text{DMF} \cdot \text{H}_2\text{O}$  (**4**). The solid line is the best-fit curve through eq 1 (see text).

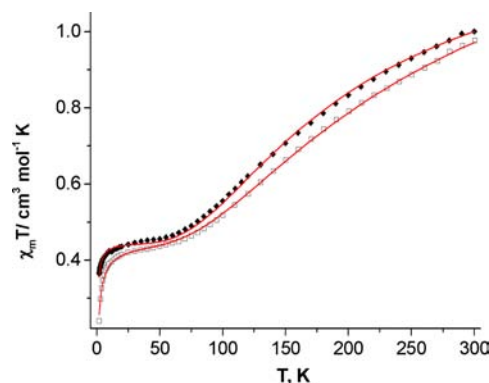
result of relatively weak antiferromagnetic interaction along axial contacts Cu(1)–O(1) ( $-x+1, -y, -z+1$ ) =  $2.513(5)$  Å, mediated by orthogonal monatomic hydroxamate oxygen bridges (O(1)–Cu(1)–O(1)\* angle is equal  $83.8(2)^\circ$ ). Due to the very long Cu...Cu ( $9.7496(18)$  Å) separations in the dinuclear molecules, the exchange interaction between these ions can only cause a minor contribution to the observed cryomagnetic behavior and, therefore, cannot condition a substantial diminishing of magnetic moment at low temperatures. Thus, the reduction of the magnetic moment of compound **4** at temperatures below 18 K might come from an antiferromagnetic interaction along the axial bonds, mediated by the monatomic hydroxamate bridges.

The magnetic behavior of **4** was analyzed with the help of a modified Bleaney–Bowers expression<sup>35</sup> for two local Cu(II) ions:

$$\chi_M = (2N\beta^2 g^2 / kT) [3 + \exp(-2J/kT)]^{-1} (1 - \rho) + \rho(2N\beta^2 g^2 S(S+1) / 3kT + 2N\alpha) \quad (3)$$

where  $2J$  is the singlet–triplet energy gap;  $g$  is the average  $g$  factor;  $2N\alpha$  refers to the temperature-independent paramagnetism;  $N$ ,  $\beta$ ,  $k$ , and  $T$  have their usual meanings; and  $\rho$  is the molar fraction of paramagnetic impurity present in the sample. Fitting of the experimental data with a least-squares technique (all the parameters were allowed to vary) gave  $J = -2.13(3) \text{ cm}^{-1}$ ,  $g = 2.085(5)$ , and  $\rho = 0.104(5)$  with  $R = 2.38 \times 10^{-4}$  (where  $R$  is the agreement factor defined as  $R = \sum_i ((\chi_{\text{obsd}})_i - (\chi_{\text{calcd}})_i)^2 / \sum_i (\chi_{\text{obsd}})_i^2$  (4)), as is shown in Figure 7.

The  $\chi T$  values observed for **1** and **5** at 300 K ( $0.977$  and  $1.010 \text{ cm}^3 \text{ K mol}^{-1}$ , respectively) are lower than the expected one for the three noninteracting copper(II) ions with  $S = 1/2$  ( $1.125 \text{ cm}^3 \text{ K mol}^{-1}$  for  $g = 2.0$ ). Upon cooling, the  $\chi T$  products gradually drop (Figure 8), which is indicative of a



**Figure 8.** Temperature dependence of  $\chi_M T$  for  $[\text{Cu}_3(\text{PicHAH})_2(\text{dipy})_2](\text{ClO}_4)_2 \cdot 4/3\text{DMSO} \cdot 2/3\text{H}_2\text{O}$  (**1**;  $\square$ ) and  $[\text{Cu}_3(\text{PyDHAH})_2(\text{tmeda})_3](\text{ClO}_4)_2$  (**5**;  $\blacklozenge$ ). The calculated values are represented by solid lines.

quite strong antiferromagnetic coupling between the copper ions in the trinuclear complexes mediated by the (N,N')-(O,O')-hydroxamate bridges and is typical of trinuclear copper(II) species with intramolecular antiferromagnetic coupling.<sup>36</sup> Note, that the  $\chi T$  product for complex **1** at 300 K and lower temperatures is smaller than that for **5**, which indicates an overall stronger antiferromagnetic coupling operating in the trinuclear core. Below 40 K, curves for both **1** and **5** reach a plateau at  $\chi T = 0.430$  and  $0.454 \text{ cm}^3 \text{ K mol}^{-1}$  for **1** and **5**, respectively, which correspond to the expected one for an  $S = 1/2$  ground spin state with  $g$  values of 2.14 and 2.20, respectively. Upon further cooling below 10 K, the  $\chi T$  values decrease again and finally at 2 K reach  $\chi T$  values  $0.240$  and  $0.367 \text{ cm}^3 \text{ K mol}^{-1}$  for **1** and **5**, respectively. The value of the  $\chi T$  product at 2 K for **1** is noticeably lower than the expected one for a resulting spin  $S = 1/2$ . The decrease observed at lower temperatures in **1** should be attributed then to weak intermolecular antiferromagnetic interactions between the trimetallic units mediated by long Cu–O and Cu–N axial contacts.

The topology of the paramagnetic centers in **1** and **5** can be considered as an isolated linear trinuclear pattern with two equivalent terminal copper(II) ions. Hence, for this case the isotropic spin Hamiltonian with two parameters of the exchange interaction:  $J_1$  (which corresponds to the interaction between the central and terminal ions) and  $J_2$  (which corresponds to the interaction between the terminal ions) can be applied:

$$H = -2J_1(S_1 \cdot S_2 + S_2 \cdot S_3) - 2J_2(S_1 \cdot S_3) \quad (5)$$

Typically, in many trinuclear complexes, the interaction between the terminal ions is very small, so the  $J_2$  parameter can be considered equal to zero and ignored. Indeed, **1** and **5** are exactly these cases, with the Cu...Cu separations between the terminal copper(II) ions equal to 9.2545(8) and 9.4273(11) Å for **1** and 9.3112(9) Å for **5**. Moreover, in **5** the terminal copper ions are separated from each other by the five-atomic bridges, which include the medial copper ion. Therefore, the quantitative interpretation of cryomagnetic behavior of **1** and **5** has been done by using an analytical expression obtained from the above-mentioned spin-Hamiltonian for the trinuclear complex with  $S_1 = S_2 = S_3 = 1/2$  [24] and  $J_2 = 0$ :

$$\chi_M = [Ng^2\beta^2/4k(T - \theta)] \times [1 + \exp(2J_1/kT) + 10 \exp(3J_1/kT)] \times [1 + \exp((2J_1)/kT) + 2 \exp(3J_1/kT)]^{-1} + N_\alpha \quad (6)$$

where  $g$  is the average  $g$  factor;  $N_\alpha$  is the temperature independent paramagnetism of copper(II) ions;  $N$ ,  $\beta$ ,  $i$ , and  $k$  have their usual meaning; and  $\theta$  is a Weiss-like correction for intermolecular interactions. The least-squares fit to the data leads to  $J_1 = -88.7(6) \text{ cm}^{-1}$ ,  $g = 2.179(5)$ , and  $\theta = -1.50(4) \text{ K}$  with  $R = 4.07 \times 10^{-4}$  for **1** and  $J_1 = -78.7(7) \text{ cm}^{-1}$ ,  $g = 2.185(5)$ , and  $\theta = -0.49(2) \text{ K}$  with  $R = 8.52 \times 10^{-5}$  for **5**.

The calculated parameters of the exchange interaction indicate the presence of a strong antiferromagnetic interaction between the neighboring copper(II) ions and a high efficiency of a superexchange interaction mediated by the hydroxamate bridges. The solid lines in Figure 8 were calculated using the above listed parameters. The small negative  $\theta$  values suggest some weak longer-range intermolecular interactions. Note that for **1** the  $\theta$  value is much larger than that for **5**, which is explained by the solid state structure of **1** where the axial Cu–O contacts are operating to form a 1-D linear polymeric chain of the trinuclear units united in triple-decked stacks (Figure 2).

## CONCLUSIONS

The copper(II) complex formation ability of two *o*-picolinehydroxamic acids, **HPicHA** and **H<sub>2</sub>PyDHA**, has been reinvestigated in an effort to obtain structural evidence of mono- and oligonuclear complexes' formation. The use of methanol/water solvent allowed us to examine the Cu(II)–**HPicHA** equilibria under homogeneous conditions between pH 1 and 11. In agreement with ESI-MS indication, the potentiometric data fitted very well with the model usually reported for copper(II) complexes of  $\alpha$ -aminohydroxamate complexes ( $[\text{CuL}]^+$ ,  $[\text{Cu}_3(\text{LH}_{-1})_4]^{2+}$ ,  $[\text{CuL}_2]$ ,  $[\text{CuL}_2\text{H}_{-1}]^-$ ), however with much higher stability of the 12-MC-4 species. The addition of a strong chelating agent to the solution dominated by the metallacrown complex resulted in isolation of the polynuclear complex of non-MC topology,  $[\text{Cu}_3(\text{PicHA-H})_2(\text{dipy})_2](\text{ClO}_4)_2 \cdot 4/3\text{DMSO} \cdot 2/3\text{H}_2\text{O}$  (**1**).

Although a very complex equilibrium occurring in the Cu(II)–**H<sub>2</sub>PyDHA** system, involving various polynuclear species of different nuclearity, hampered isolation of appropriate polynuclear complexes, the application of bidentate chelating *dipy* or *tmeda* ligands led to bi- $[\text{Cu}_2(\text{PyDHA})(\text{dipy})_2](\text{ClO}_4)_2 \cdot \text{DMF} \cdot \text{H}_2\text{O}$  (**4**) and trinuclear  $[\text{Cu}_3(\text{PyDHA-2H})(\text{tmeda})_3](\text{ClO}_4)_2$  (**5**) and  $\text{Cu}_3(\text{PyDHA-2H})(\text{dipy})_3(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (**6**) complexes.

The diversity of coordination modes observed in isolated mono-, di-, and trinuclear copper(II) complexes confirms the potential of pyridine-2-hydroxamic and pyridine-2,6-dihydroxamic acids and makes them very promising ligands in coordination chemistry.

The magnetic properties of the trinuclear complexes show a dominant antiferromagnetic coupling between the copper ions bridged by the hydroxamate groups resulting in a doublet spin ground state.

## ASSOCIATED CONTENT

### Supporting Information

Figures S1 and S2, absorption and EPR spectra of Cu(II)–**HPicHA**; Figures S3 and S4, ESI-MS of Cu(II)–**HPicHA** and Cu(II)–**H<sub>2</sub>PyDHA**; Tables S1–S7: structural details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

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