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Inorganica Chimica Acta 359 (2006) 1055–1063

Inorganica Chimica Acta

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Synthesis and reactivity of copper(II) metallacrowns with (*S*)-phenylalanine and 2-picolinehydroxamic acids

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Received 19 May 2005; received in revised form 7 October 2005; accepted 24 November 2005
Available online 4 January 2006

Abstract

The new pentanuclear 12-metallacrown-4 complexes of the formula $[Cu_5L_4]X_2$ (where H_2L is (*S*)-phenylalanine or 2-picolinehydroxamic acids and X^- is NO_3^-, Cl^-, or HSO_4^-) have been isolated in solid state for the first time and characterized by NMR and UV–Vis spectroscopy, electrospray ionization mass spectrometry and elemental analyses. The ^1H NMR spectroscopy was used to follow the transformation of these 12-metallacrown-4 complexes into lanthanide 15-metallacrown-5 complexes $[LnCu_5L_5](NO_3)_3$, and allowed to establish the correlation between the stability of the latter complexes and the lanthanide ionic radius. As indicated by ^1H NMR and ESI-MS data, the reaction of $[Cu_5L_4]X_2$ complexes with Ni^{2+} ion results in replacement of the central Cu^{2+} ion and formation of heteronuclear 12-metallacrowns-4 of the $[NiCu_4L_4]X_2$ type. The crystallization of the complex of 2-picolinehydroxamic acid, $[Cu_5(picha)_4](NO_3)_2$, in the presence of pyridine leads to destruction of the metallacrown core and formation of trinuclear complex, $[Cu_3(picha)_2(py)_5(NO_3)_2]$, whose X-ray crystal structure has been determined.

Keywords: Metallacrowns; Hydroxamic acids; Copper complexes; Crystal structure

1. Introduction

The aminohydroxamic acids are biologically important, versatile ligands, that can bind transition metal ions in various fashions, forming mono- , di- and polynuclear complexes [1,2]. They can chelate metal ions as monoanions by two oxygen atoms or by two nitrogen atoms. In the latter case, the hydroxamic nitrogen atom is deprotonated, as observed, e.g., in mononuclear complexes of pyridine-2,6-dihydroxamic acid [3]. The dianion form of aminohydroxamic acid can act as bridging ligand combining both chelation modes (Scheme 1). In some cases, the bridging abilities of aminohydroxamic acids results in the formation of cyclic polynuclear complexes called metallacrowns [2] that are inorganic analogues of crown ethers. In particular, the geometric requirements of β-aminohydroxamic acids, related to the formation of 6-membered chelate ring, lead to square arrangement of 12-metallacrown-4 [2,4]. On the other hand, the α-aminohydroxamic acids, that form only 5-membered chelate rings, prefer pentagonal arrangement of 15-metallacrown-5, as observed in the interesting heteropolynuclear copper(II)–lanthanide(III) complexes [2,5,6] such as $[LnCu_5(picha)_5](NO_3)_3$ and $[LnCu_5(pheha)_5](NO_3)_3$, (where Ln is the lanthanide(III) ion, picha is 2-picolinehydroxamic acids dianion and pheha is (*S*)-phenylalaninehydroxamic acid dianion). The latter complexes containing five copper(II) ions, discovered by Pecoraro and co-workers, are assembled in the presence of additional central metal ion such as Ln^{3+}, UO_2^{2+} or Ca^{2+}, and they correspond to complexed forms of crown ethers. The corresponding central metal free metallacrowns $[Cu_5L_5]$ have not been obtained so far. Indeed, the identity of the copper complexes, formed by α-aminohydroxamic acids without the additional template metal ion, strongly depends on the kind of hydroxamic acid and the reaction

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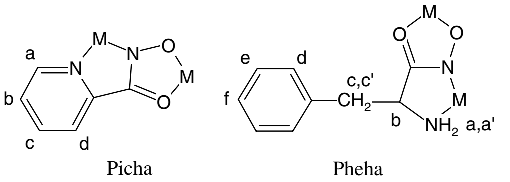
doi:10.1016/j.ica.2005.11.019



Scheme 1. The bridging chelation mode of 2-picoline and (*S*)-phenylalaninehydroxamic acids and the labeling scheme of the ligands.

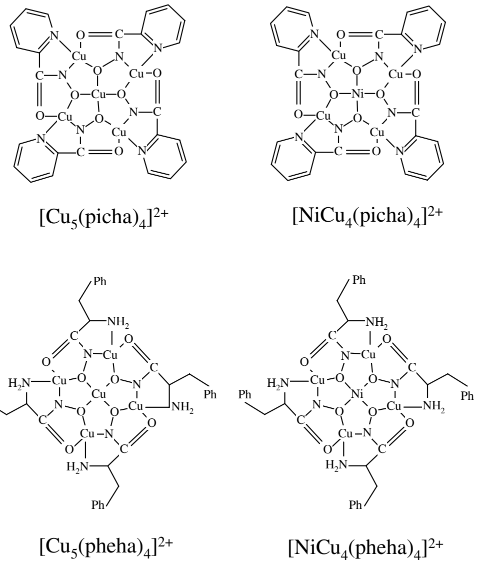
conditions. The earlier solution studies suggested the presence of mononuclear and dinuclear Cu(II) complexes of α-aminohydroxamic acids such as H_2pheha [7]. More recently Dallavalle et al. studied the complexation equilibria of (*S*)-phenylalanine and (*S*)-tryptophanhydroxamic acids [8] or other hydroxamic acids [9,10] and found that the only polynuclear complexes that can be detected in aqueous solution by ESI-MS are the pentanuclear complexes $[Cu_5L_4]^{2+}$. For these complexes a cup configuration of 12-metallacrown-4 was proposed, that corresponds to non-planar analogue of the structure of $[Cu_5L_4]^{2+}$ complexes formed by β-aminohydroxamic acids [4]. Similar results were obtained by Binnemans and coworkers who studied the complexation of copper(II) by (*S*)- and (*R*)-leucine and (*S*)-tyrosinehydroxamic acids [11]. On the basis of ESI-MS, UV–Vis, CD and NMR measurements the latter group discovered also that addition of uranyl ion to copper(II) 12-metallacrown-4 complexes results in re-assembly of these metallacrowns to a 15-matallacrowns-5. Additionally, competition studies showed that the complexation of uranyl ion within the 15-metallacrown-5 is preferred to the complexation of Ca^{2+} or Nd^{3+} [11] ions. On the other hand, the 12-metallacrown-4 complexes were not detected in the reaction of copper(II) with (*S*)-norvaline hydroxamic acid; in this case, the X-ray crystal structure of the complex isolated in the solid state showed the presence of helical polynuclear complex of the formula $[Cu_{28}L_{20}(OAc)_{10}Cl_4(MeOH)_5(H_2O)_3]$ [12].

In this article we report that $[Cu_5(pheha)_4]Cl_2$ and $[Cu_5(picha)_4]X_2$ (where X^- is NO_3^- or HSO_4^-) complexes (Scheme 2) can indeed be synthesized and isolated in solid state. We also present the ^{1}H NMR and ESI-MS solution study of the rearrangement of 12-metallacrown-4 complexes into 15-metallacrown-5 complexes triggered by addition of different Ln(III) ions, as well as of the replacement of the central Cu(II) ion in the 12-metallacrown-4 by Ni(II) ion. The X-ray crystal structure of the trinuclear $[Cu_3(picha)_2(py)_5(NO_3)_2]$ complex obtained by recrystallization of $[Cu_5(picha)_4](NO_3)_2$ in pyridine is also reported and discussed.

2. Experimental

2.1. Reagents and materials

Picolinehydroxamic acid (H_2picha) and (*S*)-phenylalaninehydroxamic acid (H_2pheha) were prepared as reported in Ref. [5]. All lanthanide(III) nitrates were obtained from Aldrich-Chemical Co., $Cu(NO_3)_2 \cdot 3H_2O$, $CuCl_2 \cdot 2H_2O$, KOH, $Ni(NO_3)_2 \cdot 6H_2O$ and methanol (POCH) were of analytical grade and used without further purification.



Scheme 2. The proposed structures of $[Cu_5L_4]^{2+}$ complexes derived from 2-picoline and (*S*)-phenylalaninehydroxamic acids and the corresponding heteronuclear copper(II)–nickel(II) complexes (the coordinated anions or solvent molecules are omitted).

2.2. Synthesis

2.2.1. Synthesis of $[LnCu_5(pheha)_5](NO_3)_3$

$[LnCu_5(pheha)_5](NO_3)_3$ complexes (Ln = La, Ce, Nd, Sm, Dy and Eu) were prepared as reported in the literature [6].

2.2.2. Synthesis of $[LnCu_5(picha)_5](NO_3)_3$ complexes

This synthesis is a modification of the synthesis reported in the literature [5]. $Cu(CH_3COO)_2$ (0.238 g, 1.19 mmol) was dissolved in methanol (20 ml). Solid 2-picolinehydroxamic acid (0.165 g, 1.19 mmol) was added, and the obtained deep brown solution was stirred for 15 min. Upon addition of solid $Sm(NO_3)_3 \cdot 6H_2O$ (0.106 g, 0.238 mmol), a green precipitate separated out after 10 min. The mixture was stirred for 2 h. The green powder was filtered off, washed with methanol and dried (yield 72%). The analogous La, Nd, Gd, Dy and Yb complexes were synthesized using the same procedure (yield: 76%, 79%, 63%, 53% and 59%, respectively). The ESI-MS spectra, as well as ^{1}H NMR spectra of DMSO-d_6 solutions of La, Nd, Sm and Gd complexes and CD_3OD solutions of Dy and Yb complexes are in agreement with the literature data [5]. The new $[CeCu_5(picha)_5](NO_3)_3 \cdot 3H_2O$ complex was obtained in the same fashion in 77% yield. *Anal.* Calc. for $CeCu_5C_{30}H_{26}N_{13}O_{22}$: C, 26.14; H, 1.90; N, 13.21. Found: C, 26.16; H, 1.62; N, 13.06%. ^{1}H NMR (DMSO-d_6, ppm): δ 11.22, 33.93, 35.24 and 88.35. The ^{1}H NMR spectrum of the DMSO-d_6 solution of Yb derivative was also recorded (ppm): δ 14.98, 40.88, 43.17, 102.04.

2.2.3. Synthesis of $[Cu_5(pheha)_4]Cl_2$

(*S*)-phenylalaninehydroxamic acid (0.107 g, 0.597 mmol) and KOH (0.067 g, 1.19 mmol) were dissolved in methanol (15 ml). A solution of $CuCl_2 \cdot 2H_2O$ (0.102 g, 0.597 mmol) in methanol (10 ml) was added dropwise under stirring, and the resulting solution was refluxed overnight. A solid product precipitated out which was filtered off, yielding the complex as a green powder (75 mg, 46%). *Anal.* Calc. for $Cu_5C_{36}H_{40}N_8O_8$ Cl_2: C, 39.24; H, 3.66; N, 10.17. Found: C, 39.48; H, 3.45; N, 9.83%. ^{1}H NMR (DMSO-d_6, ppm): δ 35.35, 22.11, 9.74, 7.20, 7.05, 6.28, −89.65 and −126.75.

2.2.4. Synthesis of $[Cu_5(picha)_4](NO_3)_2$

2-Picolinehydroxamic acid (0.082 g, 0.597 mmol) was added to a stirred solution of $(Cu(NO_3)_2 \cdot 3H_2O$ (0.144 g, 0.597 mmol) in methanol (25 ml), causing a change in colour from pale blue to deep brown. A solution of KOH (0.067 g, 1.19 mmol) in methanol (10 ml) was added dropwise under stirring, and a light green precipitate started to appear immediately. The mixture was stirred for 3 h. The resulted green precipitate was filtered, washed with acetonitrile and dried in air (120 mg, 67%). *Anal.* Calc. for $Cu_5C_{26}H_{19}N_{11}O_{14}$: C, 30.39; H, 1.86; N, 15.00. Found: C, 30.58; H, 1.95; N, 14.94%. ^{1}H NMR (CD_3OD, ppm): δ 12.55, 35.76, 36.89 and 94.5. ^{1}H NMR (DMSO-d_6, ppm): δ 12.41, 35.40, 36.24 and 90.87. ^{1}H NMR (D_2O, ppm): δ 12.38, 32.41, 34.60 and very broad signal around 82 ppm.

2.2.5. Synthesis of $[Cu_5(picha)_4](HSO_4)_2$

2-Picolinehydroxamic acid (0.165 g, 1.19 mmol) was added under stirring to a solution of $(Cu(SO_4)_2 \cdot 5H_2O$ (0.298 g, 1.19 mmol) in methanol (25 ml), causing a change in colour to deep green. After 5 min a green precipitate appeared. The mixture was stirred overnight and the obtained precipitate filtered, washed with methanol and dried (240 mg, 75%). *Anal.* Calc. for $Cu_5C_{36}H_{18}$ $N_8O_{16}S_2$: C, 27.28; H, 2.21; N, 10.61; S, 6.50. Found: C, 27.06; H, 1.72; N, 10.47; S, 6.07%. ^{1}H NMR (DMSO-d_6, ppm): δ 12.47, 35.44, 36.28 and 90.90.

2.2.6. Synthesis of $[Cu_3(picha)_2(py)_5(NO_3)_2]$ complex

$[Cu_5(picha)_4](NO_3)_2$ (30 mg, 0.030 mmol) was dissolved in 2 mL of pyridine, then 10 mL of diethyl ether was layered on top of the solution and the solution was left to stand. After 8 days, during diffusion of diethyl ether into pyridine solution, black-green single crystals of $[Cu_3(picha)_2(py)_5(NO_3)_2]$, suitable for X-ray structure analysis were formed and separated (12 mg, 40%). *Anal.* Calc. for $Cu_3C_{37}H_{35}N_{11}O_{11}$: C, 44.42; H, 3.53; N, 15.40. Found: C, 44,16; H, 3.75; N, 15.23%. ^{1}H NMR (DMSO-d_6, ppm): δ 7.62, 7.86, 9.30, 12.42, 35.37, 36.21 and 90.77.

2.3. ^{1}H NMR, ESI-MS and UV–Vis spectrophotometric measurements

The ^{1}H NMR spectra were collected on Bruker AMX 500 spectrometer. Spectra were calibrated using solvent signals as reference. The gradient-COSY and HMQC spectra were acquired using 256 × 1 K data points and zero filled to 1 K × 1 K matrix. The ^{1}H NMR method was used to follow the reaction of 12-metallacrown-4 complexes with La(III), Sm(III), Nd(III), Yb(III) and Ni(II) ions. In a typical experiment with Ln(III) ions 2.3 equivalents of the appropriate lanthanide(III) nitrate was added to 0.5 mL of DMSO-d_6 solution containing 5 mg of $[Cu_5(picha)_4](NO_3)_2$ and spectra were recorded over a period of 4 weeks. In the case of Ni(II) reaction, 3.5 or 5 equiv. of solid $(Ni(NO_3)_2 \cdot 6H_2O$ were added to 0.5 mL of DMSO-d_6 solution containing 5 mg of $[Cu_5(picha)_4](NO_3)_2$ or $[Cu_5(pheha)_4]Cl_2$. The positive mode ESI-MS spectra of methanol solutions were measured on Finnigan MAT TSQ 700 triple stage quadrupol mass spectrometer equipped with an electrospray ionization (ESI) source (flow rate 2 μl/min, capillary temp. 200 °C, the potential between the needle and the electrospray chamber 3.5 kV) or on Micromass LCT (TOF) instrument (flow rate 10 μl/min, capillary 3.5–4.5 kV, extraction cone 20–50 V, sample cone 10 V, RF lens 500 V, desolvation temp. 120 °C, source temp. 120 °C). The UV–Vis absorption spectra were recorded on CARY 5 UV–VIS–NIR spectrophotometer using matched 1 and 0.1 cm quartz cells. A stock solution of $[Cu_5(pheha)_4]Cl_2$ (1.5×10^{-4} M) was prepared in methanol–water solution (9:1-V/V) while the stock solution of $[Cu_5(picha)_4](NO_3)_2$ (1×10^{-3} M) was prepared in DMSO.

2.4. X-ray data collection and structure determination

The X-ray single crystal data were collected on a KUMA KM-4 diffractometer equipped with a two-dimensional area CCD detector on a single crystal with dimension of $0.55 \times 0.25 \times 012$ mm^3 at 100 K. Graphite-monochromatized MoKα radiation ($\lambda = 0.71073$ Å) and ω-scan technique with $\Delta\omega = 0.75°$ for one image were used. A total of 960 images for six different runs covering over 95% of the Ewald sphere were performed. The cell parameters were refined by least-squares method on the basis of 3857 reflections. One image was monitored as a standard after every 50 images for controlling the stability of the crystal. Integration of the intensities and corrections for Lorenz and polarization effects were performed using a KUMA KM-4 CCD software [13]. Face-indexed analytical absorption was calculated using SHELXTL program [14]. The minimum and maximum transmission factors are 0.4652 and 0.8306, respectively. A total of 23 377 (4874 independent, $R_{\text{int}} = 0.0533$) were integrated and used for the crystal structure determination. The structure was solved by direct methods and refined by full-matrix least-squares methods using SHELXL-97 program [15] with anisotropic thermal parameter for all non-hydrogen atoms. The H atoms of the aromatic rings were introduced in their computed coordinates (HFIX 43) with isotropic thermal parameters $U_{\mathrm{iso}}(H) = 1.2U_{\mathrm{eq}}$, i.e., 20% higher than the thermal parameters of the carbon atoms directly joined the H atom. The final difference Fourier maps showed no peaks of chemical significance. More details of data collection and final refinement parameters are listed in Table 1. Selected bond lengths and angles are summarized in Table 2.

3. Results and discussion

3.1. Synthesis and characterization of the $[Cu_5L_4]X_2$ complexes

Several attempts have been done to synthesize the pentanuclear $[Cu_5L_4]X_2$ complexes derived from 2-picoline- or (*S*)-phenylalaninehydroxamic acids (H_2L) under various conditions. In the case of 2-picolinehydroxamic acid they can be formed in various solvents (water, methanol, DMF) with different starting Cu(II) salts, and they can be isolated (in lower yields) even when aminohydroxamic acids and Cu(II) salts are reacted without added base. Best results have been obtained by reacting in methanol copper(II) salts, hydroxamic acids and 2 equiv. of base per ligand. Elemental analyses and clear ESI-MS spectra that show the expected isotope pattern (Fig. 1, Supplementary Fig. 4) confirm the identity of the complexes. Apart from the $[Cu_5L_4]^{2+}$ ion, the mass spectra exhibit $[Cu_5L_4]X^+$ ions, e.g., $\{[Cu_5(picha)_4](HSO_4)\}^+$ at 959 m/e and $\{[Cu_5(picha)_4](NO_3)\}^+$ at 924 m/e, indicating possible coordination of anions or clusterization of anions and cations during ionization process. The ESI-MS spectra of (*S*)-phenylalaninehydroxamic acid derivative show the presence of the same species observed in solution mixture by Dallavalle et al. [8].

Table 1
Crystallographic data and final refinement parameters for $Cu_3(2\text{-picha})_2(py)_5(NO_3)_2$

Chemical formula	$Cu_3C_{37}H_{33}N_{11}O_{10}$
Molecular weight	982.37
Temperature (K)	100(1)
Crystal system	monoclinic
Space group	*C*2/*c* (no. 15)
Unit cell dimensions	
a (Å)	10.383(2)
b (Å)	12.806(2)
c (Å)	31.209(4)
β (°)	99.20(2)
V (Å^3)	4096.3(9)
Z	4
D_{obs} (measured by flotation) (g cm^{-3})	1.59
D_{calc} (g cm^{-3})	1.593
Radiation, Mo Kα (Å)	0.71073
Absorption coefficient (μ/mm^{-1})	1.614
Number of measured reflections	23377
Number of independent reflections	4897 ($R_{\mathrm{int}} = 0.0533$)
Number observed reflections (>$2\sigma(I)$)	3857
Refinement on F^2	
$R\ [F^2 > 2\sigma(F^2)]$[a]	0.0481
$wR(F^2$ all reflections)[b]	0.1063
Goodness-of-fit, *S*	1.063
Residual electron density, $\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	+0.444, −0.394

[a] $R = \sum\|F_o| - \|F_c|/\sum F_o$.

[b] $wR = \{\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.0522P)^2 + 2.77P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 2
Selected geometrical parameters of $Cu_3(2\text{-picha})_2(py)_5(NO_3)_2$ complex

Cu1–O1	1.944(2)	Cu2–N1	2.006(2)
Cu1–O2	1.909(2)	Cu2–N2	2.076(2)
Cu1–N1P1	2.014(2)	Cu2–N1^i	1.979(2)
Cu1–N1P2	2.000(2)	Cu2–N2^i	2.075(2)
Cu1–O2N	2.385(2)	Cu2–N1P3	2.333(2)
O1–Cu1–O2	84.35(8)	N1–Cu2–N2	78.3(1)
N1P1–Cu1–N1P2	92.72(9)	N1–Cu2–N2^i	96.8(1)
O1–Cu1–N1P2	93.41(9)	N2–Cu2–N1^i	97.6(1)
O2–Cu1–N1P1	88.04(9)	N1^i–Cu2–N2^i	79.0(1)
O1–Cu1–O2N	97.14(7)	N1–Cu2–N1P3	104.0(1)
O2–Cu1–O2N	97.14(9)	N2–Cu2–N1P3	93.9(1)
N1P1–Cu1–O2N	88.91(8)	N1^i–Cu2–N1P3	98.1(1)
N1P2–Cu1–O2N	96.95(8)	N2^i–Cu2–N1P3	107.5(1)

Symmetry code: $i = 1/2 - x,\ 1/2 - y,\ -z$.

In the case of mononuclear octahedral, square planar of square pyramidal Cu(II) complexes the nuclear T_1 and T_2 relaxation times are very short and NMR spectra of these complexes are severely broadened and difficult to observe [16]. In the case of dinuclear and polynuclear Cu(II) complexes magnetic interactions between metal ions result in faster electronic relaxation, hence narrower ^{1}H NMR signals can be observed [16].

In the case of the ^{1}H NMR spectra of the discussed complexes the very observation of well defined NMR lines is in accordance with the presence of a polynuclear Cu(II) complex. The ^{1}H NMR spectra of these complexes are rather simple. Four lines of equal intensity are observed for picha complexes, that corresponds to one set of pyridine ring signals. This indicates that all aminohydroxamic ligands in $[Cu_5(picha)_4]^{2+}$ complexes are equivalent in accordance with the structure depicted in Scheme 2. Similarly, 8 lines of intensity 1:1:1:1:1:1:2:2 are observed for the deuterated DMSO solution of $[Cu_5(pheha)_4]Cl_2$ complex, in accordance with the presence of one type of chiral pheha ligand and diastereotopic CH_2 and NH_2 groups. The ^{1}H NMR lines can be tentatively assigned on the basis of linewidth analysis. In paramagnetic complexes with dominant dipolar and Curie relaxation mechanisms, the linewidths are inversely proportional to the sixth power of the proton–metal distance [16]. On this basis the ^{1}H NMR signals (Fig. 2) of $[Cu_5(picha)_4](NO_3)_2$ complex at 12.41, 35.40, 36.24 ppm and 90.87 ppm can be assigned to positions c, b, d and a, respectively (see Scheme 1 for the labelling scheme), and the signals of $[Cu_5(pheha)_4]Cl_2$ complex at 35.35, 22.11, 9.74, 7.20, 7.05, 6.28, −89.65 and −126.75 ppm of the intensity 1:1:1:1:2:2:1:1 can be assigned to the positions b, c, c′, d, e, f, a and a′, respectively. The two up-field signals of the latter complex disappear after

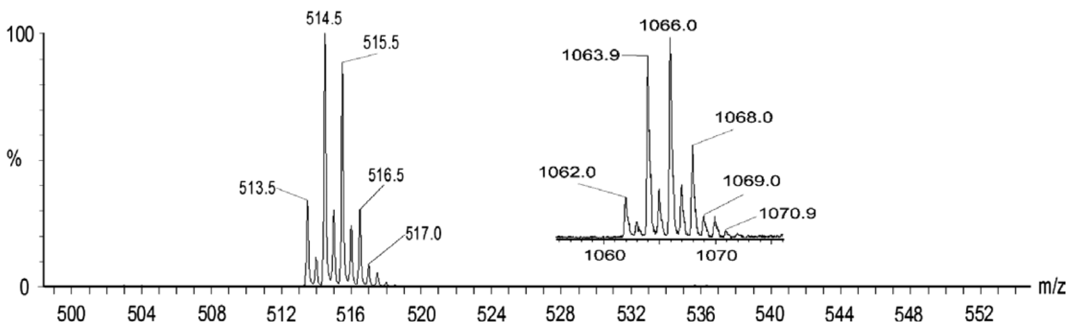


Fig. 1. Experimental ESI-MS spectrum (positive ion mode) of $[Cu_5(pheha)_4]Cl_2$ complex.

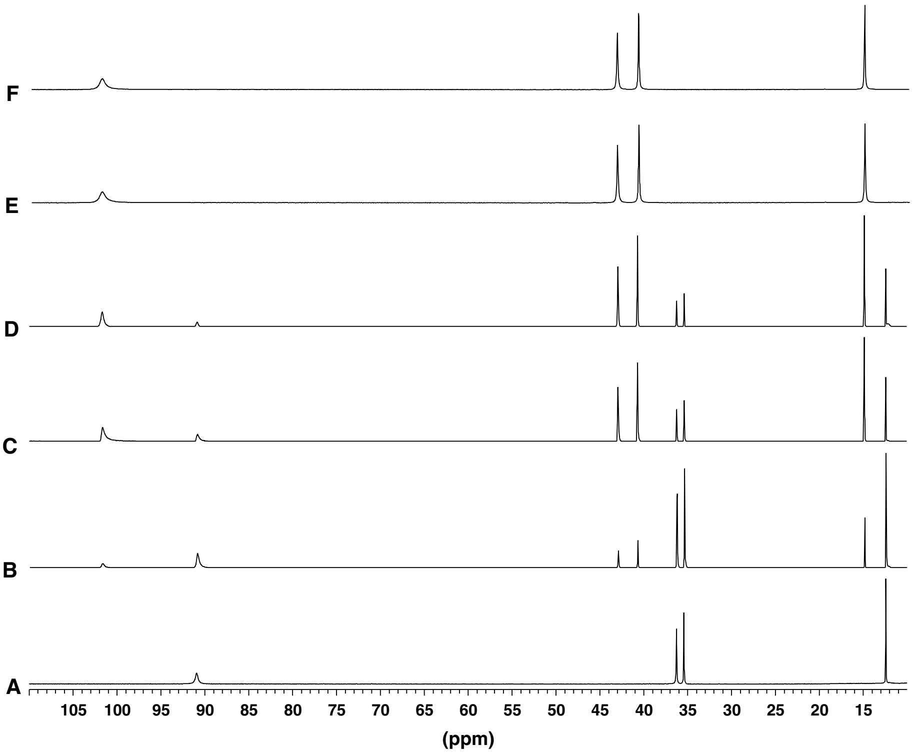


Fig. 2. ^{1}H NMR spectra (DMSO-d_6, 298 K) representing the transformation of $[Cu_5(picha)_4](NO_3)_2$ to $[YbCu_5(picha)_4](NO_3)_3$: (A) sample containing 5 mg of the starting $[Cu_5(picha)_4](NO_3)_2$ complex, (B) the same sample with 2.3 equiv. $(Yb(NO_3)_3 \cdot 5H_2O$ added, recorded after 1 h, (C) after one day, (D) after 2 weeks, (E) after 30 days. (F) Sample of the independently synthesized $[YbCu_5(picha)_4](NO_3)_3$.

addition of D_2O because they correspond to exchangeable NH_2 protons. The up-field paramagnetic shifts of the NH_2 protons reflect probably different relative contributions of the contact and dipolar shifts to the isotropic shift in comparison with the down-field shifts of other protons. The signals of the two diastereotopic β protons are well separated as expected for paramagnetic complex. The above assignments are confirmed by 2D NMR spectra, although some of the expected correlations corresponding to broad signals were not observed due to fast nuclear relaxation. The COSY spectrum of $[Cu_5(picha)_4](NO_3)_2$ show correlations between signals c and b, as well as between c and d, while the COSY spectrum of $[Cu_5(pheha)_4]Cl_2$ show strong correlation between signals of geminal protons c and c′, in addition to weak correlation between b and c′. The assignment of the geminal pair c and c′ is unequivocally confirmed by the HMQC spectrum (Supplementary Fig. 1), since both signals are correlated to the same carbon 13 signal.

It should be noted that for the analogous complex of leucinehydroxamic acid, generated in solution using equimolar amount of the ligand and copper(II) acetate, no peaks attributable to the ligand could be observed in ^{1}H NMR spectrum. It was suggested that this effect can result from the relatively long electronic relaxation times of the non-planar Cu(II) ion [11]. For better comparison we have generated complexes of 2-picoline- and (*S*)-phenylalaninehydroxamic acids using equimolar amounts of the ligand and copper(II) acetate in CD_3OD, or copper(II) nitrate in DMSO-d_6. In the case of the discussed ligands we were able to observe ^{1}H NMR spectra of paramagnetic complexes generated in situ. The spectra are solvent, counteranion and time dependent and only in the case of 2-picolinehydroxamic acid the signals of 12-metallacrown-4 complex are clearly seen (along with the signals of other species). These data show that formation of 12-metallacrown-4 complexes is not a simple and fast process. Thus the difference in NMR behaviour of the 12-metalacrown-4 complexes with the various aminohydroxamic acids may reflect subtle geometry differences that strongly influence the magnetic exchange between the Cu(II) ions and relaxation rates. It is also possible that for the complexes generated in situ, chemical exchange, related to binding of anions, protonation or interconversion of various polynuclear complexes, may influence the NMR spectra leading in extreme cases to broadening of signals beyond detection.

The UV–Vis spectra of 1.5×10^{-4} M $[Cu_5(pheha)_4]Cl_2$ complex in methanol–water (9:1-V/V) solution show bands at 636 and 350 nm, while a DMSO solution of 1×10^{-3} M $[Cu_5(picha)_4](NO_3)_2$ complex exhibit two bands at 705 and 360(sh) nm. The bands at 636 and 705 are in the region of d–d transitions and are characteristic for species in which the metal ion is bound to two nitrogen atoms of the ligand [4,7], while bands at 350 and 360 (Sh) are corresponding to the charge-transfer transitions [4]. The UV–Vis spectrum of $[Cu_5(pheha)_4]Cl_2$ complex (Supplementary Fig. 2) corresponds well to the theoretical spectrum calculated by Dallavalle and Tegoni [8], thus confirming that the same $[Cu_5L_4]^{2+}$ complex was observed in potentiometric and spectrophotometric titrations.

3.2. Reactions of $[Cu_5L_4]X_2$ complexes with Ln(III) and Ni(II) ions

^{1}H NMR spectroscopy was also used to study the solution reactivity of $[Cu_5L_4]X_2$ complexes in transmetallation reactions. Addition of lanthanide(III) nitrate salts to DMSO-d_6 solutions of $[Cu_5(picha)_4](NO_3)_2$ or $[Cu_5(pheha)_4]Cl_2$ results in slow disappearance of signals of the starting complexes and growth of ^{1}H NMR signals of the lanthanide 15-metallacrown-5 complexes $[LnCu_5(picha)_5](NO_3)_3$ and $[LnCu_5(pheha)_4](NO_3)_3$, respectively (Fig. 2). Thus the α-aminohydroxamic acid complexes of copper(II) can rearrange according to reaction [17]:

$$5Cu_5L_4^{2+} + 4Ln^{3+} \leftrightarrow 4[LnCu_5L_5]^{3+} + 5Cu^{2+}$$

Similar rearrangement was observed for the complex of leucinehydroxamic acid in the reaction with the uranyl ion [11]. The above reactions with Ln(III) ions are practically completed after about 30 days at room temperature and 2 days at 323 K. The reaction is reversible for complexes of smaller (heavier) lanthanide(III), as observed by addition of Cu(II) salts to DMSO solutions of Sm(III), Dy(III) and Yb(III) $[LnCu_5(picha)_5](NO_3)_3$ complexes. In this case slow growth of NMR signals of $[Cu_5(picha)_4](NO_3)_2$ complex is observed as well as of signals of unknown minor byproduct complex. For the larger (lighter) lanthanide ions such as La(III), Ce(III) and Nd(III) the above reaction is strongly shifted to the right and a reverse reaction is not observed. In this way the metathesis reaction allows for estimation of relative stability of $[LnCu_5(picha)_5]^{3+}$ complexes. It is clear that the stability of the complexes decreases along the series of the lanthanide(III) ions. This series corresponds to increasing Lewis acidity and electrostatic interaction with the ligands of Ln(III) ions, and decreasing ion radius. The higher stability $[LnCu_5(picha)_5]^{3+}$ complexes of lighter Ln(III) ions can be explained on the basis of a better fit between the size of the core of the "free" $[Cu_5(picha)_5]$ metallamacrocycle and the size of larger lanthanide(III) ions.

$[Cu_5(pheha)_4]Cl_2$ complex was also reacted with $(Ni(NO_3)_2 \cdot 6H_2O$. Addition of nickel(II) nitrate (3.5 or 5 equiv.) to DMSO-d_6 solution of $[Cu_5(pheha)_4]Cl_2$ results in gradual appearance of only one new set of eight new ^{1}H NMR signals (Fig. 3) at 40.00, 16.70, 9.01, 7.38, 7.29, 7.02, −65.79 and −95.70 ppm. Similarly, after addition of nickel(II) nitrate to $[Cu_5(picha)_4](NO_3)_2$ or $[Cu_5(picha)_4](HSO_4)_2$ solution, a new set of four signals at 68.00, 25.75, 25.25 and 11.65 ppm is observed. In both cases, the general spectrum pattern is similar to that of the starting copper complex and the number of signals correspond to one type of coordinated hydroxamate ligand. The new signals observed are not present in the NMR spectra of Ni(II)/H_2L or HL^- solutions. Another control experiment, where copper(II) nitrate was used in place of nickel(II) nitrate, confirmed that the observed spectral changes do not arise from binding of additional anion ligand. Thus, the new complexes generated in solution have to be mixed Ni(II)–Cu(II) species. In principle, one can expect formation of the series of heteropolynuclear complexes of the general formula $[Cu_xNi_{5-x}L_4]^{2+}$ that can be formed after exchange of Cu(II) ions by Ni(II) ions in $[Cu_5L_4]^{2+}$ complexes. The observed spectral patterns are in accord with the formation of mixed Cu(II)–Ni(II) complexes of high symmetry. Two mixed Cu(II)/Ni(II) 12-metallacrowns-4 can exhibit one set of aminohydroxamate signals, that is $[NiCu_4L_4]^{2+}$ complexes with Ni(II) ion in the centre (Scheme 2), or $[Ni_4CuL_4]^{2+}$ complexes with Cu(II) ion in the centre. In principle, mixed polynuclear complexes of lower symmetry may exhibit one set of NMR signals in the situation of fast (on the NMR time scale) dissociation of the complex and averaging of the aminohydroxamate signals. Such a dynamic exchange of the aminohydroxamate ligands is not in accord with the observation of separate NMR signals of the starting $[Cu_5L_4]^{2+}$complexes (Fig. 3). The final conformation of the identity of the mixed metallacrown complex is based on ESI-MS (Supplementary Figs. 3 and 4). The isotopic patterns of the signals of the diluted NMR samples correspond to sum of the signals derived from $[NiCu_4L_4]^{2+}$ and $[Cu_5L_4]^{2+}$complexes, present in the same ratio as determined by integration of ^{1}H NMR signals.

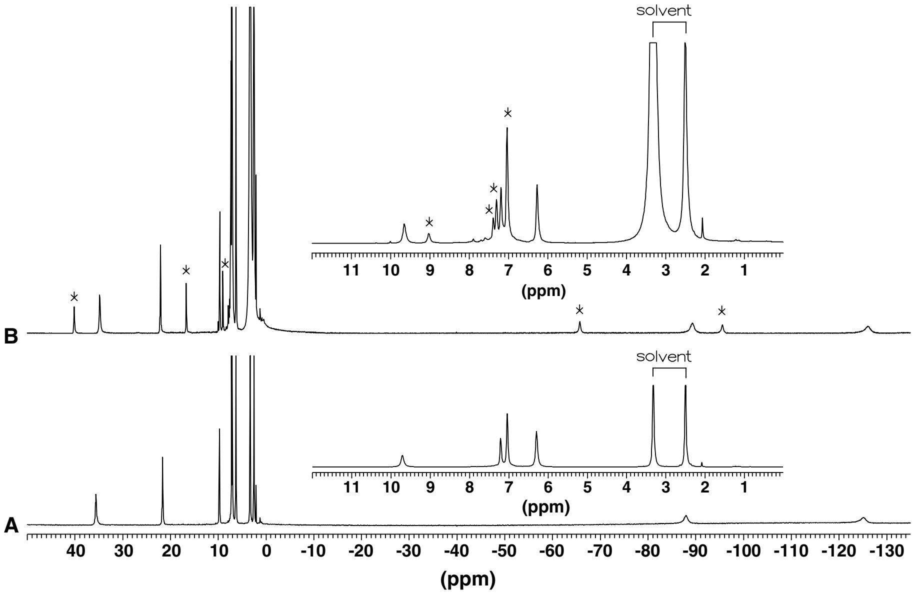


Fig. 3. (A) ^{1}H NMR spectrum (DMSO-d_6, 298 K) of $[Cu_5(pheha)_4]Cl_2$, (B) spectrum obtained after the addition of 3.5 equiv. of $Ni(NO_3)_2 \cdot 6H_2O$ after one month. (∗) refer to the signals corresponding to $[NiCu_4(pheha)_4]^{2+}$.

3.3. Characterization and X-ray crystal structure of $[Cu_3(picha)_2(py)_5(NO_3)_2]$ complex

When $[Cu_5(picha)_4](NO_3)_2$ complex is crystallized from the pyridine/diethyl ether solvent, black-green crystals of trinuclear complex $[Cu_3(picha)_2(py)_5(NO_3)_2]$ are obtained. For longer crystallization times, besides these crystals of $[Cu_3(picha)_2(py)_5(NO_3)_2]$ complex, the blue crystals of $[Cu(py)_4](NO_3)_2 \cdot 2py$ [18] are also formed. This latter complex is also obtained by slow evaporation of $[Cu_5(picha)_4](NO_3)_2$ solution in neat pyridine. The ^{1}H NMR spectrum of DMSO-d_6 solution of the crystals of $[Cu_3(picha)_2(py)_5(NO_3)_2]$ indicate the presence of only one type of complex giving rise to four resonances of the coordinated 2-picolinehydroxamate at 12.42, 35.37, 36.21 and 90.77 ppm in addition to three averaged signals of the coordinated pyridine molecules at 7.62, 7.86 and 9.30 ppm. On the other hand, when the reaction of the starting $[Cu_5(picha)_4](NO_3)_2$ complex with pyridine or deuterated pyridine is followed by ^{1}H NMR, complicated spectra are observed, that do not correspond to the simple dissociation of the starting pentanuclear complex and formation of the final product. The ESI-MS spectra of methanol solution of the crystals of the trinuclear complex surprisingly show signals at 431 m/e (base) and 924 m/e (52% of base) corresponding to the starting complex $[Cu_5(picha)_4](NO_3)_2$. This result reflects dissociation of the coordinated pyridine in diluted solution, followed by the rearrangement of the trinuclear complex to the preferred pentanuclear one. The above observations taken together reflect competition between 2-picolinehydroxamate ligand and pyridine for the copper(II) ions.

Refinement of the crystal structure established that half of the molecule of trinuclear copper complex is independent. Additionally, the refinement shows that the central Cu(II) ion (Cu2) is disordered, i.e., it is statistically distributed over two symmetrically equivalent positions. The disordering of the Cu2 ion implicates the disordering of the pyridine molecule that is joined to it. Additionally, this pyridine molecule is located at the inversion centre, i.e., only half of this pyridine molecule is independent. Thus, in the crystal, the molecule of trinuclear copper complex has two statistical orientations (Fig. 4). An inversion center relate these two orientations of the molecule.

The three copper ions in $[Cu_3(picha)_2(py)_5(NO_3)_2]$ complex are connected by the two bridging 2-picolinehydroxamate ligands. Both of those ligands coordinate the central copper(II) ion by two nitrogen atoms and outer copper(II) ion by two oxygen atoms. Each Cu of the three Cu(II) atoms of $[Cu_3(picha)_2(py)_5(NO_3)_2]$ has a square pyramidal coordination. Both peripheral, symmetry equivalent, Cu(II) atoms have the same coordination. They are coordinated in square equatorial positions by two oxygen atoms of chelating 2-picolinehydroxamate ligand and by two N atoms of two pyridine molecules, while in the axial position they are coordinated by one of the oxygen atoms of the nitrate groups. The central disordered Cu(II) atom is coordinated in equatorial positions by four N atoms of two trans-oriented chelating 2-picolinehydroxamate anionic ligands and in the axial position by N atom of pyridine molecule (see Fig. 4). The Cu1 atom is displaced by 0.172(1) Å from the equatorial plane defined by four atoms (N and O) in square coordination, while the central copper atom (Cu2) of this trinuclear complex is more displaced (0.384(1) Å) from the equatorial plane defined by the four N atoms of two 2-picolinehydroxamate(2-) anions. The rings of pyridine molecules joined to the peripheral copper atom (Cu1) are inclined by angles of 50.2(1)° (the ring of

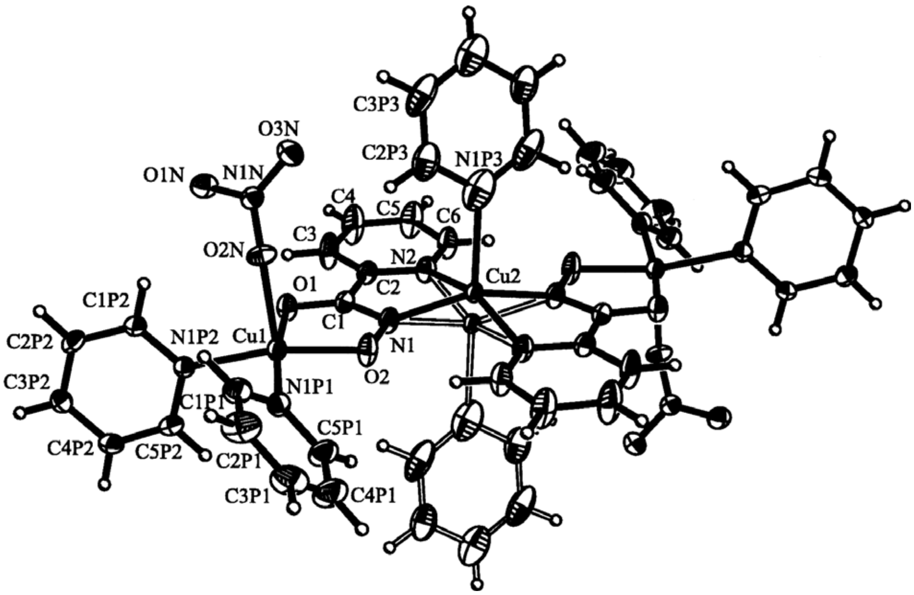


Fig. 4. View of $[Cu_3(picha)_2(py)_5(NO_3)_2]$ molecule with the labelling scheme showing its two orientations in the crystal. The atoms joined together by black-sticks of the bonds illustrate one of the two orientations of the molecule, the second orientation, related to the different location of the central Cu2 atom is illustrated as the open-sticks of the bonds. Displacement ellipsoids are shown at the 50% probability level.

N1P1···C5P1) and 88.5(1)° (the ring of N1P2···C5P2). The planar NO_3^- ion that coordinates to Cu1 by O2N atom is inclined by 51.8(1)° to the equatorial plane defined by four atoms equatorially joined to Cu1. The equatorial Cu–N and Cu–O bonds are shorter by ~0.35 Å than the axial Cu–N and Cu–O bonds (see Table 2). The equatorial angle of O1–Cu1–O2 due to the chelating effect of the 2-picolinehydroxamate ligand is smaller than 90°, while the N–Cu1–N angle involving pyridine molecules is greater than 90° due to the interaction between the pyridine rings. Two equatorial N–Cu2–N angles involving both N atoms of the same chelating 2-picolinehydroxamate ligand are smaller, and two N–Cu2–N angles involving N atoms of two chelating 2-picolinehydroxamate ligands are greater than 90°. The planes defined by the equatorially coordinated atoms to Cu1 and Cu2 atoms are inclined by an angle of 7.8(1)°. The ring of pyridine molecule coordinated to the central Cu2 atom is almost perpendicular to the equatorial plane (88.8(1)°), while the orientation of the ring describes well the torsion angle of N1–Cu2–N1P3–C2P3 that equals to 6.8(1)°. The distance between the Cu(II) atoms in this trinuclear complex is equal to 4.684(2) Å.

In the crystal, the arrangement of $[Cu_3(picha)_2(py)_5(NO_3)_2]$ molecules is mainly determined by the intermolecular van der Waals interaction and electrostatic interactions between the positively charged Cu(II) atoms and the oxygen atoms of the NO_3^- groups. As was mentioned above the molecule in the crystal has two symmetrically equivalent orientations that differ in the location of the central Cu2 atom and pyridine molecule joined to it. Since the pyridine molecule joined to the central copper atom is located on an inversion center, thus the carbon and nitrogen atoms occupy statistically the ring positions 1,4 (0.5 by carbon and 0.5 by nitrogen). The molecules of this trinuclear complex form pseudo one-dimensional chains that are alternatively parallel and perpendicular to the (1 1 0) plane (see Supplementary Fig. 5).

4. Conclusions

The new types of copper(II) complexes with aminohydroxamic acids have been isolated in solid state for the first time, i.e., pentanuclear 12-metallacrown-4 complexes and a linear trinuclear complex. In the presence of additional metal ions of large diameter, such as a lanthanide(III) ion, the former complexes rearrange to 15-metallacrowns-5, while in the presence of nickel(II) ion, the 12-metallacrown-4 structure is retained and the Ni(II) is bound in the central position.

Appendix A. Supplementary data

Crystallographic data, details on the data collection and refinement have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 268720. Copies of this material may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005.11.019.

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