

Synthesis and Structural Characterisation of Copper(II) 15-Metallacrown-5 Complexes with Pb^{II}, Hg^{II}, Ag^I, Na^I and Y^{III} Central Metal Ions

Sabry Hamed Seda,^[a] Jan Janczak,^[b] and Jerzy Lisowski*^[a]

Keywords: Metallamacrocyles / Hydroxamic acids / Lead / Mercury / Copper / Crystal structure

The new copper(II) 15-metallacrown-5 complexes with the central metal ions Pb^{II}, Hg^{II}, Ag^I, Na^I and Y^{III}, with the formula [MCu₅L₅]X_n (H₂L is 2-picolinedihydroxamic acid or (S)-phenylalaninedihydroxamic acid and X[−] is NO₃[−] or Cl[−]), have been synthesised and characterised by NMR and UV/Vis spectroscopy, electrospray mass spectrometry and elemental analysis. The Pb^{II}- and Hg^{II} 15-metallacrown-5 complexes were obtained in the crystalline form as pyridine adducts [PbCu₅(picha)₅(py)₆](NO₃)₂·3(py) and [HgCu₅(picha)₅(py)₇](NO₃)₂·2(py) and their X-ray crystal structures were determined. In both complexes, each peripheral Cu^{II} ion of the metallacrown is coordinated by one pyridine molecule

bonded in the axial position. In the case of the Pb^{II} derivative, one additional axial pyridine molecule is bound to the central metal ion, while in the case of the Hg^{II} derivative, two axial pyridine ligands are bound to the central Hg^{II} ion. The relative stability of the copper(II) 15-metallacrown-5 complexes with various central metal ions was determined on the basis of competition reactions. The relative preference of the 15-metallacrown-5 system for the central metal ion follows the series Na^I, Ag^I < lanthanide(III), Hg^{II} < Pb^{II}.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

Introduction

The bridging properties of aminohydroxamate ligands are the basis for the formation of cyclic polynuclear complexes called metallacrowns,^[1] which are inorganic analogues of crown ethers. In particular, the geometric requirements of the α -aminohydroximates, that form only five-membered chelate rings, result in a pentagonal arrangement of the 15-metallacrown-5 system (Figure 1), as observed in the interesting heteropolynuclear copper(II)–lanthanide(III) complexes^[2–5] such as [LnCu₅(picha)₅](NO₃)₃ and [LnCu₅(pheha)₅](NO₃)₃, {where Ln is the lanthanide(III) ion, picha is the 2-picolinedihydroxamic acid dianion and pheha is the (S)-phenylalaninedihydroxamic acid dianion (Figure 2)} or analogous uranyl(VI) and calcium(II) complexes.^[6] These complexes, which contain five copper(II) ions and which were discovered by the Pecoraro group, are assembled in the presence of an additional central metal ion, i.e. Ln³⁺, UO₂²⁺ or Ca²⁺, and they correspond to complexed forms of crown ethers. In contrast, without the additional metal template, the same α -aminohydroxamic acids form the [Cu₅L₄]X₂ 12-metallacrown-4 complexes.^[7,8] Analogous 15-metallacrown-5 lanthanide(III) complexes in

which the peripheral Cu^{II} ions are replaced by Ni^{II} ions^[9] or the α -aminohydroxamate ligand is replaced by mandelohydroximate^[10] (Figure 2) are also known. The high stability and preferred binding of UO₂²⁺ over Ca²⁺ by the copper(II) 15-metallacrown-5 complexes were studied in the context of the sequestering of the toxic uranyl ions and the biological importance of hydroxamic acids.^[8a] The α -aminohydroxamic acids alone were also studied as possible sequestering agents for toxic lead(II) ions.^[11]

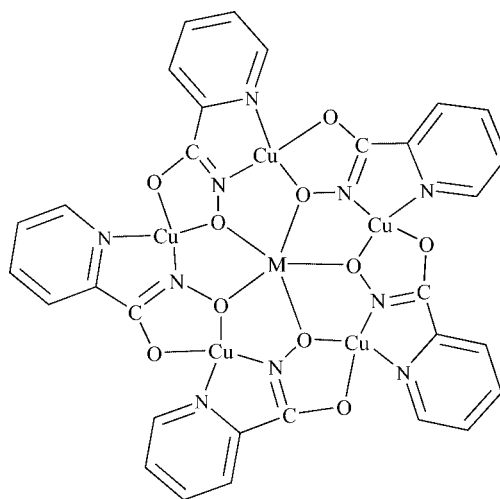


Figure 1. The structure of the [MCu₅(picha)₅]ⁿ⁺ 15-metallacrown-5 complex. Axial ligands are omitted.

[a] Department of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland
Fax: +48-71-3282-348

E-mail: jurekl@wchuw.chem.uni.wroc.pl

[b] Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P. O. Box 1410, 50-950 Wrocław, Poland

Supporting information for this article is available on the WWW under <http://www.eurjic.org> or from the author.

In this contribution, we present the synthesis, spectroscopic and structural characterisation of [MCu₅L₅]X_n 15-

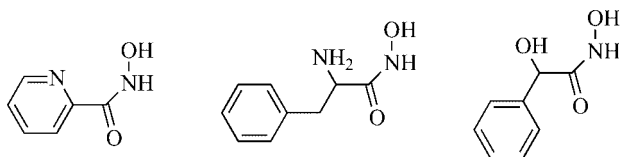


Figure 2. 2-Picoline-, phenylalanine- and mandelohydroxamic acids.

metallacrown-5 complexes (Figure 1) with new central metal ions [$M = \text{Pb}^{\text{II}}$, Hg^{II} , Ag^{I} , Na^{I} or Y^{III} , $L = \text{picha}$ or pheha , $X = \text{NO}_3^-$ or Cl^-] and demonstrate the high stability of the 15-metallacrown-5 complexes of toxic lead(II) and mercury(II) metal ions.

Results and Discussion

X-ray Crystal Structure of the $[\text{PbCu}_5(\text{picha})_5(\text{py})_6](\text{NO}_3)_2 \cdot 3(\text{py})$ Complex

The slow diffusion of diethyl ether into a pyridine solution of the $[\text{PbCu}_5(\text{picha})_5](\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ complex results in the formation of crystals of the pyridine adduct $[\text{PbCu}_5(\text{picha})_5(\text{py})_6](\text{NO}_3)_2 \cdot 3(\text{py})$. The asymmetric unit of this complex contains the cationic complex $[\text{PbCu}_5(\text{picha})_5(\text{py})_6]^{2+}$ (Figure 3). The 15-metallacrown-5 system formed by five Cu^{II} ions and five bridging 2-picolinehydroximate anions in this complex is less planar (the deviation of the atoms from the mean equatorial plane ranges from $-1.061 \text{ \AA}$ for C43 to $+0.804 \text{ \AA}$ for O41) relative to that in other copper(II) 15-metallacrown-5 complexes.^[2–6] The buckling of the metallacrown most likely results from the relatively large size of the Pb^{II} ion. Two of the 2-picolinehydroximate fragments are tilted with respect to the plane formed by the remaining three 2-picolinehydroximate ligands in such a way that the diameter of the ring formed by the five hydroximate oxygen atoms increases. The cavity radius of the metallacrown is $1.15 \text{ \AA}$ and matches well with the radius of the six-coordinate Pb^{II} ion ($1.19 \text{ \AA}$). Each copper(II) ion is equatorially coordinated by two O atoms [the Cu–O distances range from 1.908 to $1.989(3) \text{ \AA}$] and two N atoms [the Cu–N distances range from 1.941 to $2.030(3) \text{ \AA}$] of the two neighbouring 2-picolinehydroximate ligands and one axial pyridine molecule [the Cu– N_{py} distances range from 2.289 to $2.416(4) \text{ \AA}$]. Thus, the complex has a pseudo fivefold symmetry. In this way, all five copper(II) ions exhibit identical coordination environments, in contrast to previously reported copper(II) 15-metallacrown-5 complexes,^[2–6] which exhibit a variation in the axial donor sets of the copper(II) ions. The Pb^{II} ion is coordinated in the centre of the metallacrown by five hydroximate oxygen atoms [the Pb–O distances range from 2.491 to $2.590(3) \text{ \AA}$] and is additionally coordinated by one axial pyridine molecule with a Pb– N_{py} bond length of $2.493(3) \text{ \AA}$. Interestingly, this pyridine molecule and all five pyridine molecules coordinated to the Cu^{II} ions are positioned on the same side of the macrocycle. Moreover, the pyridine-rich faces of the neighbouring complex cations related by an inversion centre are directed

towards each other, which results in the formation of layers of pyridine molecules almost parallel to the (020) crystallographic plane (see Figure 4). In the unit cell, two of the three additional pyridine solvate molecules are located on the other side of the 15-metallacrown-5 core and one of the two is located almost perpendicularly to the core and is oriented with the N atom pointing towards the Cu4 atom [the $\text{Cu4} \cdots \text{N}_{\text{py}}$ contact is $2.752(3) \text{ \AA}$]. The third pyridine solvate molecule is located in the same plane as the coordinated pyridine molecules.

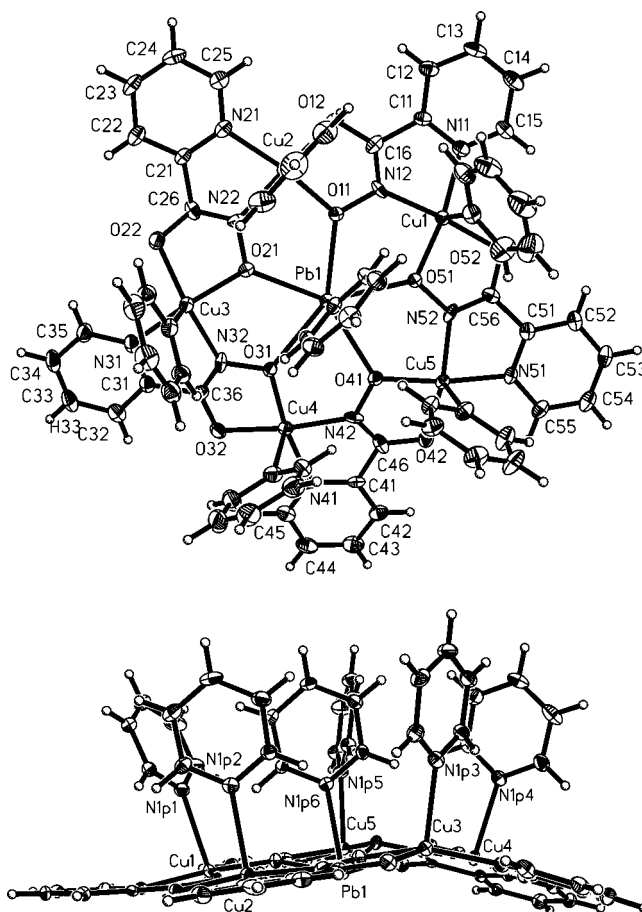


Figure 3. Top and side view of the $[\text{PbCu}_5(\text{picha})_5(\text{py})_6]^{2+}$ complex cation.

The Pb^{II} ion adopts a pentagonal-pyramidal geometry, which is similar to that observed in a related nickel(II) 15-metallacrown-5 complex.^[9] This geometry is relatively rare for lead(II) complexes.^[12,13] The arrangement of the donor atoms around the Pb^{II} ion is hemi-directed, in accord with the presence of the stereochemically active lone pair of electrons.^[14] The Pb^{II} ion is slightly displaced by $0.476(2) \text{ \AA}$ from the mean plane formed by the five hydroximate oxygen atoms in a direction away from the bound pyridine ligand. As a result of this displacement towards the open face, the Pb^{II} ion adopts an umbrella-like structure.^[12,13] The displacement of the Pb^{II} ion towards the stereochemically active lone pair and the resulting distortion of the pentagonal pyramid is in accord with the VSEPR model, which predicts the privileged position of the lone pair.^[15]

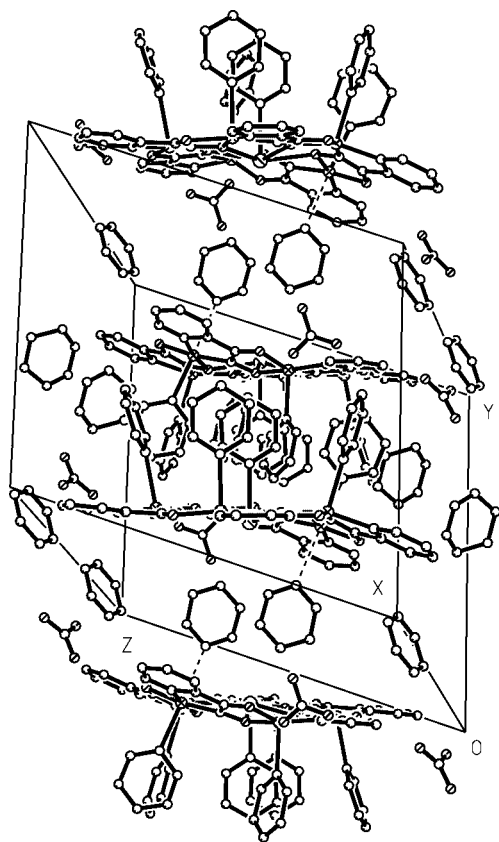


Figure 4. View of the crystal packing of $[\text{PbCu}_5(\text{picha})_5(\text{py})_6](\text{NO}_3)_2 \cdot 3(\text{py})$ showing layers of pyridine molecules almost parallel to the (020) crystallographic plane.

X-ray Crystal Structure of the $[\text{HgCu}_5(\text{picha})_5(\text{py})_7](\text{NO}_3)_2 \cdot 2(\text{py})$ Complex

The slow diffusion of diethyl ether into a pyridine solution of the $[\text{HgCu}_5(\text{picha})_5](\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ complex also results in the formation of a pyridine adduct, $[\text{HgCu}_5(\text{picha})_5(\text{py})_7](\text{NO}_3)_2 \cdot 2(\text{py})$. The asymmetric unit of this crystal contains the cationic complex $[\text{HgCu}_5(\text{picha})_5(\text{py})_7]^{2+}$ (Figure 5). The central Hg^{II} ion is positioned almost exactly in the least-squares plane of the five oxygen donor atoms of the metallacrown [deviation from this plane is equal to 0.071(3) Å]. This ion is seven-coordinate – the five equatorial oxygen atoms of the metallacrown [the Hg–O distances range from 2.533 to 2.568(2) Å] and the two nitrogen atoms of the axially coordinated pyridine molecules [the two Hg–N_{py} distances are equal to 2.175(3) and 2.182(3) Å] define a pentagonal-bipyramidal geometry. While several mercury(II) complexes of highly distorted pentagonal-bipyramidal geometry are known,^[16] the discussed complex presents the first example of Hg^{II} complexes that forms an almost regular pentagonal bipyramid with a fivefold symmetry (Supporting Information, Table S1). Each copper(II) ion in $[\text{HgCu}_5(\text{picha})_5(\text{py})_7]^{2+}$ is equatorially coordinated by two O atoms [the Cu–O distances range from 1.914 to 1.994(2) Å] and two N atoms [the Cu–N distances range from 1.928 to 2.043(3) Å] of the two neighbouring 2-picolinedihydroxamate ligands and one axial pyridine molecule

[the Cu–N_{py} distances range from 2.256 to 2.275(3) Å]. Similarly, as in the lead(II) complex discussed above, all the pyridine molecules axially coordinated to the Cu^{II} ions are positioned on the same side of the metallacrown.

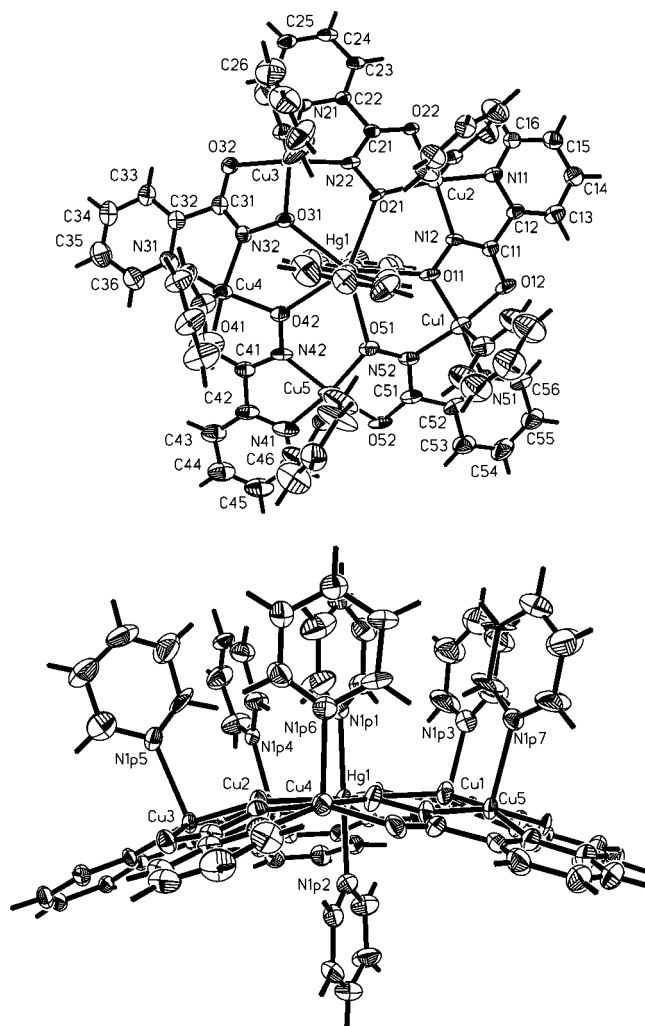


Figure 5. Top and side view of the $[\text{HgCu}_5(\text{picha})_5(\text{py})_7]^{2+}$ complex cation.

The deviation of the copper(II) 15-metallacrown-5 system from planarity in this complex is the largest for this class of compounds. The metallacrown adjusts itself to the size of the central Hg^{II} ion by adopting a distinctive bowl shape. The cavity radius of the metallacrown further increases to 1.20 Å, which reflects the large effective size of the central mercury(II) ion. A search of the Cambridge Structural Database (Version 5.24) for Hg complexes containing a similar N_2O_5 donor set yields only one complex, bis[(μ2-trifluoroacetato-*O,O,O'*)-(trifluoroacetato-*O,O'*)pyridinemercury(II)] with a highly distorted pentagonal-bipyramidal geometry.^[16a] The latter complex contains five equatorially coordinated oxygen atoms and two axially coordinated pyridine molecules with Hg–O distances that range from 2.55 to 2.87 Å and an average Hg–N_{py} distance of 2.12 Å. These values, which are somewhat similar to those observed in $[\text{HgCu}_5(\text{picha})_5(\text{py})_7](\text{NO}_3)_2 \cdot 2(\text{py})$, indi-

cate that the effective “equatorial” radius of mercury(II) in this type of environment is substantially larger than the 1.02 and 1.14 Å reported for six- and eight-coordinate mercury(II) complexes, respectively.^[17] Even longer bonds with equatorial donor atoms are found in mercury(II) complexes that have other donor sets and that exhibit a distorted pentagonal-bipyramidal geometry.^[16] Thus, the seven-coordinate mercury(II) ion is large enough to push aside the aminohydroxamate ligands and force the 15-metallacrown-5 system to adopt a bowl shape. The variation in the cavity radius reflects the flexibility of the copper(II) 15-metallacrown-5 ring in adjusting to the geometric requirements of the central metal ion.

In the unit cell, the pyridine solvate molecules are located in the hole between the cationic $[\text{HgCu}_5(\text{picha})_5(\text{py})_7]^{2+}$ complexes related by an inversion centre and translation (see Supporting Information, Figure S1). The two charge-compensating nitrate anions are also located in this hole. The pyridine-rich faces of the neighbouring complex cations related by an inversion centre form a layer of pyridine molecules almost parallel to the (230) crystallographic plane.

Synthesis and Solution Characterization of the $[\text{MCu}_5\text{L}_5]\text{X}_n$ Complexes

The 15-metallacrown-5 complexes with the Pb^{II} , Hg^{II} , Ag^{I} , Na^{I} and Y^{III} central metal ions can be obtained in high yields in a straightforward synthesis based on the self assembly of α -aminohydroxamic acid, Cu^{II} ions and the central metal ion in the presence of base. The NMR spectroscopic and ESI MS analyses of the crude reaction mixtures show that the 15-metallacrown-5 complex is the main product. In the case of the Ag^{I} complex, the product isolated in the synthesis based on stoichiometric amounts of substrates exhibits small amounts of other complexes, and the use of excess Ag^{I} ions was necessary for the isolation of the pure product. It is interesting to note the profound differences in product formation when NaOH or KOH was used in the reaction with α -aminohydroxamic acid and Cu^{II} ions. While the smaller sodium cation templates the formation of the 15-metallacrown-5 ring, the potassium cation is too big to fit in the centre of this metallacrown, and the 12-metallacrown-4 complex with a central Cu^{II} ion is therefore formed.^[7]

The identities of the new copper(II) 15-metallacrown-5 complexes, $[\text{NaCu}_5(\text{picha})_5](\text{NO}_3)$, $[\text{AgCu}_5(\text{picha})_5](\text{NO}_3)$, $[\text{PbCu}_5(\text{picha})_5](\text{NO}_3)_2$, $[\text{PbCu}_5(\text{pheha})_5](\text{NO}_3)_2$, $[\text{HgCu}_5(\text{picha})_5](\text{NO}_3)_2$ and $[\text{YCu}_5(\text{pheha})_5]\text{Cl}_3$, are confirmed by positive mode ESI MS analysis in methanol/DMSO solutions. The spectra of the two lead(II) complexes exhibit peaks at $m/z = 1266$ and 602 corresponding to the $\{[\text{PbCu}_5(\text{picha})_5](\text{NO}_3)\}^+$ and $[\text{PbCu}_5(\text{picha})_5]^{2+}$ species, respectively (Supporting Information, Figure S2), or a peak at $m/z = 707$ corresponding to $[\text{PbCu}_5(\text{pheha})_5]^{2+}$ (Supporting Information, Figure S3). The ESI-MS spectrum of the mercury(II) complex reveals peaks at $m/z = 1260$ and 599

corresponding to $\{[\text{HgCu}_5(\text{picha})_5](\text{NO}_3)\}^+$ and $[\text{HgCu}_5(\text{picha})_5]^{2+}$, respectively, in addition to the signals of unidentified species that are formed by rearrangement of the starting complex in diluted solution. In the case of the yttrium(III) complex, signals at $m/z = 1368$, 666 and 432 corresponding to the $\{[\text{YCu}_5(\text{pheha})_5](\text{Cl})_2\}^+$, $\{[\text{YCu}_5(\text{pheha})_5](\text{Cl})\}^{2+}$ and $[\text{YCu}_5(\text{pheha})_5]^{3+}$ species, respectively, were observed in its spectrum, while only one signal is observed for both the silver(I) and sodium(I) 15-metallacrown-5 complexes; $m/z = 1107$ for $[\text{AgCu}_5(\text{picha})_5]^+$ and $m/z = 1021$ for $[\text{NaCu}_5(\text{picha})_5]^+$.

The positions of copper(II) d–d bands of the discussed 15-metallacrown complexes are sensitive to the type of central metal ion. This effect may reflect changes in axial ligation and/or in the degree of distortion from the ideal geometry (e.g. square pyramidal) of the copper(II) ions, which results from the slightly different buckling of the 15-metallacrown-5 system in each complex. The UV/Vis spectra of DMSO solutions of the Na^{I} , Hg^{II} and Pb^{II} complexes derived from picolinehydroxamic acid show bands at 558, 592 and 622 nm, respectively, and the spectra of the Pb^{II} and Yb^{III} complexes derived from (*S*)-phenylalaninehydroxamic acid exhibit d–d bands at 547 and 573 nm, respectively.

The ^1H NMR spectra of the $[\text{D}_6]\text{DMSO}$ solutions of the 15-metallacrown-5 complexes derived from 2-picolinehydroxamic acid each exhibit four signals (Figure 6), while those of the derivatives of (*S*)-phenylalaninehydroxamic acid show six non-exchangeable signals (Supporting Information, Figure S4) in addition to two proton-exchangeable signals, in accord with the presence of diastereotopic CH_2 and NH_2 groups. The ^1H NMR signals 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.^[18] On this basis, the broadest and most-downfield-shifted ^1H NMR signals of the $[\text{MCu}_5(\text{picha})_5](\text{NO}_3)_x$ complexes can be assigned to the protons at position 6 of the picoline ring, the two signals in the 20–40 ppm region correspond to those at positions 3 and 5 and the relatively narrow signals around 10 ppm correspond to those at position 4. In the case of the Pb^{II} derivative, this assignment was confirmed by the observation of correlations between the signals for the protons at positions 3 and 4 and between the signals for those at positions 5 and 4 (in other cases, the nuclear relaxation was too fast to observe the expected COSY correlations). In the case of the $[\text{MCu}_5(\text{pheha})_5]\text{X}_n$ complexes, the most-downfield-shifted ^1H NMR signals correspond to the protons at the α position, the next two signals correspond to those at the β positions, the three relatively narrow signals around 7 ppm are assigned to the protons of the phenyl ring and the two very broad upfield-shifted signals to the NH_2 protons. The two upfield-shifted signals disappear after addition of D_2O because they correspond to exchangeable protons. The signals for the two diastereotopic β protons are well separated as expected for paramagnetic complexes. The ^1H NMR spectral patterns of the discussed $[\text{MCu}_5\text{L}_5]^{n+}$ complexes are very similar to those of the anal-

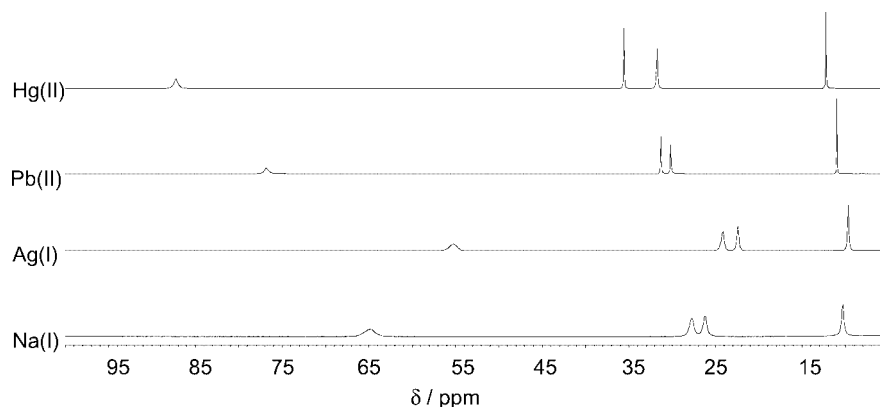


Figure 6. ^1H NMR spectra (298 K) of $[\text{D}_6]\text{DMSO}$ solutions of the $[\text{NaCu}_5(\text{picha})_5](\text{NO}_3)$, $[\text{AgCu}_5(\text{picha})_5](\text{NO}_3)$, $[\text{PbCu}_5(\text{picha})_5](\text{NO}_3)_2$ and $[\text{HgCu}_5(\text{picha})_5](\text{NO}_3)_2$ 15-metallacrown-5 complexes.

ogous $[\text{MNi}_5\text{L}_5]^{n+}$ and $[\text{Cu}_5\text{L}_4]^{2+}$ complexes,^[7,9] which is in accord with the dominant contact contribution to the isotropic (paramagnetic) shifts of the aminohydroximate ligand. The upfield paramagnetic shifts of the NH_2 protons probably reflect sizeable dipolar contributions to the isotropic shift or spin polarisation effects,^[18] which lead to a different sign of the contact shift of the NH_2 protons relative to those of other ligand protons.

The simple NMR spectra of the metallacrown complexes, in terms of the number of lines expected for a single α -aminohydroximate ligand, may arise as a result of two possibilities: (i) the presence of a single, pure complex of high symmetry with equivalent aminohydroximate ligands, or (ii) the presence of kinetically labile complexes of low symmetry or a mixture of labile complexes. In the latter case, the dissociation and rearrangement of the metallacrown complexes may lead to fast ligand exchange on the NMR time scale and observation of only one set of averaged signals. However, in the present case this situation can be excluded, since separate NMR signals for various α -aminohydroximate complexes are indeed observed for solutions of crude reaction mixtures or for the less-pure preparations of the discussed metallacrowns. Similarly, separate signals for the two ligand types are observed for the solutions containing mixtures of two 15-metallacrown-5 complexes with different central metal ions. Thus, the simplicity of the observed NMR spectra proves that only one complex with a high, effective fivefold symmetry is present in each case.

^1H NMR spectroscopy was used to compare the relative stabilities of the 15-metallacrown-5 complexes with various central metal ions. In the competition experiments, the additional metal salt was combined with the $[\text{D}_6]\text{DMSO}$ solutions of the 15-metallacrown-5 complexes, and the ^1H NMR spectra recorded over a period of time were used to monitor the exchange of the central metal ion. In the case of copper(II) 15-metallacrown-5 complexes with Na^+ or Ag^+ central metal ions, the addition of one equivalent of $\text{Pb}(\text{NO}_3)_2$ resulted in the disappearance of the ^1H NMR signals corresponding to the starting complexes $[\text{NaCu}_5(\text{picha})_5]^+$ or $[\text{AgCu}_5(\text{picha})_5]^+$ and the appearance of new

four signals at positions identical to those observed for $[\text{D}_6]\text{DMSO}$ solution of $[\text{PbCu}_5(\text{picha})_5](\text{NO}_3)_2$. The reaction was relatively fast (the transformation was completed after 15 min) and no intermediate was detected. Similarly, after 5 d at 323 K, complete conversion of the Na^+ - or Ag^+ 15-metallacrown-5 complexes into $[\text{LnCu}_5(\text{picha})_5]^{3+}$ ($\text{Ln} = \text{La}, \text{Sm}$) was observed after addition of one equivalent of the nitrate salt of a light lanthanide(III) ion (Figure 7, Supporting Information, Figure S5). The final spectra were identical to those of the independently synthesised $[\text{LnCu}_5(\text{picha})_5]^{3+}$ complexes. In the same reaction with heavier lanthanide(III) ions ($\text{Ln} = \text{Sm}, \text{Yb}$), a small amount of the pentanuclear $[\text{Cu}_5(\text{picha})_4]^{2+}$ 12-metallacrown-4 complex^[7] was formed, which was detected in the final NMR spectra (Supporting Information, Figures S6 and S7). The slightly different behaviour of the heavy and light lanthanide(III) ions is related to the higher stability of the copper(II) 15-metallacrown-5 complex with the lighter lanthanide(III) ions.^[7] The preference for the larger (lighter) lanthanide ions can be further confirmed by competition reactions between lanthanide(III) 15-metallacrown-5 derivatives and various lanthanide(III) salts. Addition of one equivalent of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ to a DMSO solution of $[\text{YbCu}_5(\text{picha})_5]^{3+}$ results in the gradual growth of a new signals corresponding to $[\text{LaCu}_5(\text{picha})_5]^{3+}$ or $[\text{SmCu}_5(\text{picha})_5]^{3+}$, respectively (Supporting Information, Figures S8 and S9). A partial conversion was obtained after the solution was heated for 55 d at 323 K (70% of the starting complex was converted in the case of La^{III} and 63% in the case of Sm^{III}). The reverse reactions were not observed in analogous ^1H NMR measurements. These observations indicate that the exchange of the lanthanide(III) ions is very slow, and equilibrium is not reached in these experiments. A similar situation was observed for the reaction of lanthanide(III) 15-metallacrown-5 complexes with the lead(II) nitrate. The partial (40–70%) conversion of the $[\text{LnCu}_5(\text{picha})_5]^{3+}$ complex into $[\text{PbCu}_5(\text{picha})_5]^{2+}$ was observed (Figure 8, Supporting Information, Figures S10–S12). Partial conversion of $[\text{LnCu}_5(\text{picha})_5]^{3+}$ into the corresponding mercury(II) 15-metallacrown-5 complex, $[\text{HgCu}_5(\text{picha})_5]^{2+}$, was also observed in the reaction with the mer-

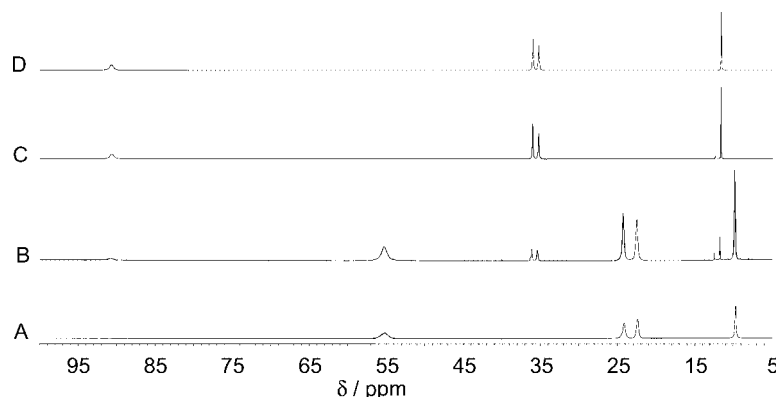


Figure 7. The ^1H NMR spectra ($[\text{D}_6]\text{DMSO}$, 298 K) of: (A) the $[\text{AgCu}_5(\text{picha})_5]^+$ complex, (B) $[\text{AgCu}_5(\text{picha})_5]^+$ treated at 323 K with 1 equiv. $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ for 1 h, (C) for 5 d, (D) the $[\text{SmCu}_5(\text{picha})_5]^{3+}$ complex.

cury(II) nitrate. In this case, however, a more complicated behaviour was observed – the subsequent decomposition of the resulting complex upon prolonged heating.

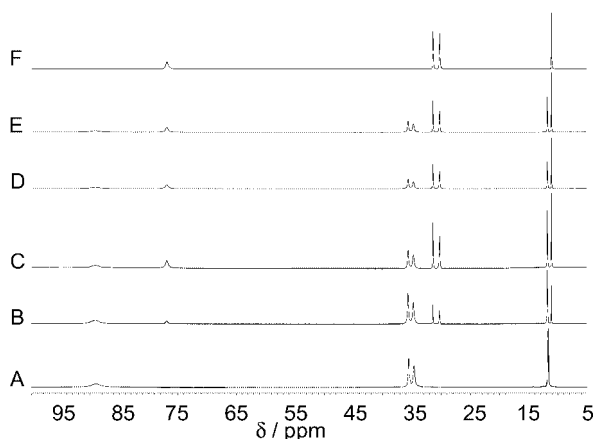


Figure 8. The ^1H NMR spectra ($[\text{D}_6]\text{DMSO}$, 298 K) of: (A) the $[\text{LaCu}_5(\text{picha})_5]^{3+}$ complex, (B) $[\text{LaCu}_5(\text{picha})_5]^{3+}$ treated at 323 K with 1 equiv. $\text{Pb}(\text{NO}_3)_2$ for 1 d, (C) for one week, (D) for two weeks, (E) for one month, (F) the $[\text{PbCu}_5(\text{picha})_5]^{2+}$ complex.

It should also be noted that the copper(II) 15-metallacrown-5 system is more stable than the copper(II) 12-metallacrown-4 system. The ring system of the 15-metallacrown-5 complex with the central Pb^{II} or Hg^{II} metal ion is not destroyed in pyridine solutions, while the 12-metallacrown-4 ring of $[\text{Cu}_5(\text{picha})_4](\text{NO}_3)_2$ is destroyed by the competing pyridine ligand.^[7] Further, the $[\text{Cu}_5(\text{picha})_4]^{2+}$ complex is converted into $[\text{MCu}_5(\text{picha})_5]^{n+}$ complexes after the addition of Ag^{I} , Pb^{II} or Hg^{II} nitrate, as indicated by ^1H NMR spectra.

Conclusions

We have shown that the copper(II) 15-metallacrown-5 system is well suited for the binding of a variety of relatively large metal ions in the centre of the metallacrown. In particular, the heavy metal ions lead(II) and mercury(II) form stable complexes of this type. In pyridine solution, these complexes form pyridine adducts, $[\text{HgCu}_5(\text{picha})_5(\text{py})_7]$ -

$(\text{NO}_3)_2$ and $[\text{PbCu}_5(\text{picha})_5(\text{py})_6](\text{NO}_3)_2$, in which the pyridine molecules are bound to the Cu^{II} ions on the same side of the metallacrown. The 15-metallacrown-5 ring can adopt a buckled conformation in order to adjust to the size and coordination requirements of the central metal ion. The relative preference of the 15-metallacrown-5 system for the central metal ion follows the series $\text{Na}^{\text{I}}, \text{Ag}^{\text{I}} < \text{lanthanide(III)}, \text{Hg}^{\text{II}} < \text{Pb}^{\text{II}}$. This series indicates that both electronic factors (preference for the metal ions that form strong bonds with the nitrogen and oxygen donor atoms) and geometric factors (preference for the larger metal ions) influence the stability of the formed complexes.

Experimental Section

Reagents and Materials

2-Picolinehydroxamic acid (H_2picha) and (*S*)-phenylalaninehydroxamic acid (H_2pheha) were prepared as reported previously.^[4] All lanthanide(III) nitrates were obtained from Aldrich Chemical Co., $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, NaOH , $\text{Pb}(\text{NO}_3)_2$, $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, pyridine and methanol (obtained from POCH) were of analytical grade and used without further purification.

Synthesis

$[\text{NaCu}_5(\text{picha})_5](\text{NO}_3) \cdot 3\text{H}_2\text{O}$: NaOH (0.095 g, 2.39 mmol) was added to a methanolic solution (25 mL) of 2-picolinehydroxamic acid (0.165 g, 1.19 mmol), and the resultant mixture was stirred for 10 min until a clear solution was obtained. A methanolic solution (10 mL) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1.19 mmol, 0.288 g) was added, and a brown precipitate, which appeared immediately, was separated. The product was recrystallised from methanol to give a deep brown complex $[\text{NaCu}_5(\text{picha})_5](\text{NO}_3) \cdot 3\text{H}_2\text{O}$ (90 mg, 33% yield). $\text{C}_{30}\text{H}_{26}\text{Cu}_5\text{N}_{11}\text{NaO}_{16}$ (1137.31): calcd. C 31.70, H 2.30, N 13.56; found C 31.38, H 1.99, N 13.48%. ^1H NMR (DMSO): δ = 9.90, 25.60, 27.42, 64.13 ppm; (CD_3OD): δ = 10.29, 26.19, 27.70, 64.82 ppm.

$[\text{AgCu}_5(\text{picha})_5](\text{NO}_3) \cdot 5\text{H}_2\text{O}$: Solid NaOH (0.048 g, 1.19 mmol) was added to a solution of 2-picolinehydroxamic acid (0.165 g, 1.19 mmol) in methanol (25 mL), and the resultant clear solution was stirred for 10 min. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.144 g, 0.597 mmol) and solid $\text{Ag}(\text{NO}_3)$ (0.041 g, 0.238 mmol) were then added, and a brown precipitate started to appear. The solution mixture was stirred for 2 d. The obtained brown precipitate was filtered and dissolved in

methanol again. Addition of a second portion of $\text{Ag}(\text{NO}_3)$ (0.02 g) to the methanol solution resulted in the formation of a brown-black precipitate, which was filtered and dried (81 mg 27% yield). $\text{C}_{30}\text{H}_{30}\text{AgCu}_5\text{N}_{11}\text{O}_{18}$ (1258.22): calcd. C 28.63, H 2.4, N 12.25; found C 28.49, H 2.38, N 12.35. ^1H NMR (DMSO): δ = 9.66, 22.38, 24.11, 55.25 ppm.

[PbCu₅(picha)₅](NO₃)₂·3H₂O: 2-picolinehydroxamic acid (0.082 g, 0.60 mmol) was added to a methanolic solution (25 mL) of $\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$ (0.120 g, 0.60 mmol), and the resultant deep brown solution was stirred for 10 min. A hot methanolic solution (10 mL) of $\text{Pb}(\text{NO}_3)_2$ (0.040 g, 0.12 mmol) was then added, and the green solution was left to stir overnight. The volume was reduced by a rotary evaporator, and the brown precipitate was filtered and dried (102 mg, 62% yield). $\text{C}_{30}\text{H}_{26}\text{Cu}_5\text{N}_{12}\text{O}_{19}\text{Pb}$ (1383.53): calcd. C 26.04, H 1.89, N 12.15; found C 26.17, H 1.72, N 12.19%. ^1H NMR (DMSO): δ = 10.98, 31.15, 31.27, 76.79 ppm.

[PbCu₅(pheha)₅](NO₃)₂·5H₂O: $\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$ (0.120 g, 0.60 mmol) was dissolved in methanol (25 mL), (*S*)-phenylalaninehydroxamic acid (0.107 g, 0.60 mmol) was added, and the mixture was stirred for 15 min. A hot methanolic solution (10 mL) of $\text{Pb}(\text{NO}_3)_2$ (0.040 g, 0.12 mmol) was then added, and the green solution was left to stir for 2 h. After evaporation of solvent, a brown precipitate was obtained (117 mg, 60% yield). $\text{C}_{45}\text{H}_{60}\text{Cu}_5\text{N}_{12}\text{O}_{21}\text{Pb}$ (1629.96): calcd. C 33.15, H 3.71, N 10.31; found C 32.96, H 3.60, N 10.31%. ^1H NMR (DMSO): δ = 6.87, 7.00, 7.15, 7.90, 14.20, 21.52, −83.61, −98.96 ppm.

[HgCu₅(picha)₅](NO₃)₂·5H₂O: $\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$ (0.120 g, 0.60 mmol) was dissolved in methanol (25 mL), 2-picolinehydroxamic acid (0.082 g, 0.60 mmol) was added, and the resultant solution was stirred for 15 min. A hot methanolic solution (10 mL) of $\text{Hg}(\text{NO}_3)_2$ (0.041 g, 0.12 mmol) was then added dropwise whilst stirring, and the resultant solution was heated at reflux overnight. The green-orange product that formed was filtered, washed with methanol and dried (91 mg, 54% yield). $\text{C}_{30}\text{H}_{30}\text{Cu}_5\text{HgN}_{12}\text{O}_{21}$ (1412.83): calcd. C 25.49, H 2.14, N 11.89; found C 25.65, H 1.76, N 11.55%. ^1H NMR (DMSO): δ = 12.24, 31.74, 35.53, 87.25 ppm.

[YCu₅(pheha)₅Cl₃·12H₂O: (*S*)-phenylalaninehydroxamic acid (0.107 g, 0.60 mmol) was added to a stirred solution of $\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$ (0.120 g, 0.60 mmol) in H_2O (25 mL). An aqueous solution (10 mL) of YCl_3 (0.033 g, 12 mmol) was added dropwise whilst stirring, and the colour of the mixture changed from green to deep blue. The mixture was left to stir overnight. Deep blue crystals of the complex were obtained (87 mg, 45% yield) upon slow evaporation of the solvent. $\text{C}_{45}\text{H}_{74}\text{Cl}_3\text{Cu}_5\text{N}_{10}\text{O}_{22}\text{Y}$ (1620.12): calcd. C 33.35, H 4.60, N 8.30; found C 33.06, H 4.60, N, 8.64%. ^1H NMR (CD_3OD): δ = 7.05, 7.26, 7.34, 9.69, 16.64, 30.38 ppm.

[LnCu₅(picha)₅](NO₃)₃ Complexes: These were synthesised as described previously.^[4,7]

^1H NMR, ESI-MS and UV/Vis Measurements

The ^1H NMR spectra were collected on a Bruker AMX 500 spectrometer. The spectra were calibrated by using solvent signals as reference. The gradient-COSY spectra were acquired with $256 \times 1\text{K}$ data points and zero-filled to $1\text{K} \times 1\text{K}$ matrix. The positive-mode ESI-MS spectra were measured with a Finnigan MAT TSQ 700 triple stage quadrupole mass spectrometer equipped with an electrospray ionization (ESI) source and with a Micromass LCT (TOF) instrument. The UV/Vis absorption spectra were measured with a CARY 5 spectrophotometer. The elemental analyses were carried out on a Perkin–Elmer 2400 CHN elemental analyzer.

X-ray Data Collection and Structure Determination

X-ray intensity data for both crystals were collected by using graphite monochromated Mo-K_α radiation on a four-circle κ -geometry KUMA KM-4 diffractometer with a two-dimensional area CCD detector at 100(2) K. The ω -scan technique with $\Delta\omega = 0.75^\circ$ for each image was used for the data collection; 960 images for six different runs covering about 98% of the Ewald sphere were performed. Initially the lattice parameters were refined on about 150 reflections obtained from 40 images for eight runs with different orientations in the reciprocal space. Finally, the lattice parameters were refined by least-squares methods based on all the reflections with $I > 2\sigma(F^2)$. One image was used as a standard for monitoring

Table 1. Crystal data for the $[\text{PbCu}_5(\text{picha})_5(\text{py})_6](\text{NO}_3)_2\cdot 3(\text{py})$ and $[\text{HgCu}_5(\text{picha})_5(\text{py})_7](\text{NO}_3)_2\cdot 2(\text{py})$ complexes.^[a]

Formula	$(\text{C}_{60}\text{H}_{50}\text{N}_{16}\text{O}_{10}\text{Cu}_5\text{Pb})(\text{NO}_3)_2\cdot 3(\text{C}_5\text{H}_5\text{N})$	$(\text{C}_{65}\text{H}_{55}\text{N}_{17}\text{O}_{10}\text{Cu}_5\text{Hg})(\text{NO}_3)_2\cdot 2(\text{C}_5\text{H}_5\text{N})$
Molecular weight	2041.37	2034.77
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> , <i>b</i> , <i>c</i> [Å]	15.676(3), 16.030(3), 17.978(3)	13.419(3), 15.077(3), 21.671(4)
α , β , γ [°]	72.29(3), 74.19(3), 79.06(3)	89.56(3), 93.84(3), 93.32(3)
Volume, <i>V</i> [Å ³]	3883.7(15)	4367.9(12)
<i>Z</i>	2	2
Temperature [K]	100(2)	100(2)
<i>D</i> _{calcd.} [g cm ^{−3}]	1.746	1.546
<i>D</i> _{obs.} (floatation) [g cm ^{−3}]	1.74	1.54
Radiation, Mo- <i>K</i> _α [Å]	0.71073	0.71073
Index range	−20 ≤ <i>h</i> ≤ 20, −21 ≤ <i>k</i> ≤ 19, −22 ≤ <i>l</i> ≤ 22	−17 ≤ <i>h</i> ≤ 17, −19 ≤ <i>k</i> ≤ 19, −28 ≤ <i>l</i> ≤ 26
Reflections collected	24344	26103
Independent reflections	17793 (<i>R</i> _{int} = 0.0214)	20822 (<i>R</i> _{int} = 0.0609)
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	14514	12327
Abs. coeff., μ [mm ^{−1}]	3.586	3.019
Correction	Lorenz and polarisation, absorption	Lorenz and polarisation, absorption
<i>T</i> _{min} , <i>T</i> _{max}	0.327, 0.678	0.526, 0.684
<i>R</i> (<i>F</i> ² > σ)	0.0365	0.0701
<i>wR</i> (<i>F</i> ² all reflections)	0.0903	0.1771
<i>S</i>	1.005	1.074
Δρ [e Å ^{−3}]	−0.941, +1.544	−1.050, +1.832

[a] $R = \sum |F_o| - |F_c| / \sum F_o$; $wR(F^2) = \{\sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4\}^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (0.0560P)^2]$ for the Pb compound and $w^{-1} = [\sigma^2(F_o^2) + (0.105P)^2]$ for the Hg compound, $P = (F_o^2 + 2F_c^2)/3$.

the stability of the crystals as well as for monitoring the data collection after every 40 images, and no correction on the relative intensity variation was necessary. Integration of the intensities and correction for Lorenz and polarisation effects were performed with a KUMA KM-4 CCD program system.^[19] The face-indexed analytical absorption was calculated with the SHELXTL program.^[20] The structures were solved by direct methods by using SHELXS of the SHELXL97 program.^[21] The structures were refined with anisotropic thermal parameters for all non-hydrogen atoms. Difference Fourier maps gave electron density concentrations located approximately for all hydrogen atom positions; these positions were idealised (HFIX 43 for all H atoms of the pyridyl rings with isotropic thermal parameters of 1.2U_{eq} of the carbon atoms joined directly to the hydrogen atoms). Final difference Fourier maps showed no peaks of chemical significance. Details of the data collection parameters and final agreement factors are presented in Table 1. Selected bond lengths are listed in the Supporting Information, Table S1. CCDC-620938 and -620939 contains the supplementary crystallographic data for the [PbCu₅(picha)₅(py)₆](NO₃)·3(py) and [HgCu₅(picha)₅(py)₇](NO₃)·2(py) complexes, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

Supporting Information (see footnote on the first page of this article): Figure S1 – crystal packing of the [HgCu₅(picha)₅(py)₇](NO₃)·2(py) complex, Figures S2 and S3 – ESI MS spectra of Pb^{II} derivatives, Figures S4–S12 – NMR spectra, and Table S1 – selected geometrical parameters for the [PbCu₅(picha)₅(py)₆](NO₃)·3(py) and [HgCu₅(picha)₅(py)₇](NO₃)·2(py) complexes are presented.

- [1] J. J. Bodwin, A. D. Cutland, R. G. Malkani, V. L. Pecoraro, *Coord. Chem. Rev.* **2001**, *216*, 489.
- [2] a) A. D. Cutland, R. G. Malkani, J. W. Kampf, V. L. Pecoraro, *Angew. Chem. Int. Ed.* **2000**, *39*, 2689; b) A. J. Stemmler, A. Barwinski, M. J. Baldwin, V. Yung, V. L. Pecoraro, *J. Am. Chem. Soc.* **1996**, *118*, 11962.
- [3] a) A. D. Cutland, J. A. Halfen, J. W. Kampf, V. L. Pecoraro, *J. Am. Chem. Soc.* **2001**, *123*, 6211; b) A. D. Cutland-Van Nord, J. W. Kampf, V. L. Pecoraro, *Angew. Chem. Int. Ed.* **2002**, *41*, 4668; c) C. M. Zaleski, E. C. Depperman, J. W. Kampf, M. L. Kirk, V. L. Pecoraro, *Inorg. Chem.* **2006**, *45*, 10022.
- [4] A. J. Stemmler, J. W. Kampf, M. L. Kirk, B. H. Atasi, V. L. Pecoraro, *Inorg. Chem.* **1999**, *38*, 2807.
- [5] T. N. Parac-Vogt, A. Pacco, P. Nockemann, S. Laurent, R. N. Muller, M. Wickleder, G. Meyer, L. Vander Elst, K. Binnemans, *Chem. Eur. J.* **2006**, *12*, 204.
- [6] A. J. Stemmler, J. W. Kampf, V. L. Pecoraro, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2841.
- [7] S. H. Seda, J. Janczak, J. Lisowski, *Inorg. Chim. Acta* **2006**, *359*, 1055.
- [8] a) T. N. Parac-Vogt, A. Pacco, C. Görrler-Walrand, K. Binnemans, *J. Inorg. Biochem.* **2005**, *99*, 497; b) A. Pacco, T. N. Parac-Vogt, E. van Basien, K. Pierloot, C. Görrler-Walrand, K. Binnemans, *Eur. J. Inorg. Chem.* **2005**, 3303; c) M. Careri, F. Dallavalle, M. Tegoni, I. Zagnoni, *J. Inorg. Biochem.* **2003**, *93*, 174; d) M. Tegoni, F. Dallavalle, B. Belosi, M. Remelli, *Dalton Trans.* **2004**, 1329.
- [9] S. H. Seda, J. Janczak, J. Lisowski, *Inorg. Chem. Commun.* **2006**, *9*, 792.
- [10] T. N. Parac-Vogt, A. Pacco, P. Nockemann, Y.-F. Yuan, C. Görrler-Walrand, K. Binnemans, *Eur. J. Inorg. Chem.* **2006**, 1466.
- [11] D. Batka, E. Farkas, *J. Inorg. Biochem.* **2006**, *100*, 2.
- [12] B. Sui, W. Zhao, G. Ma, T. Okamura, J. Fan, Y.-Z. Li, S.-H. Tang, W.-Y. Sun, N. Ueyama, *J. Mater. Chem.* **2004**, *14*, 1631.
- [13] M. Yamami, H. Furutachi, T. Yokoyama, H. Okawa, *Inorg. Chem.* **1998**, *37*, 6832.
- [14] L. Shimon-Livny, J. P. Glusker, C. W. Bock, *Inorg. Chem.* **1998**, *37*, 1853.
- [15] R. J. Gillespie, *Chem. Soc. Rev.* **1992**, *21*, 59–69.
- [16] a) J. Halfpenny, R. W. H. Small, F. G. Thorpe, *Acta Crystallogr., Sect. B* **1978**, *34*, 3075; b) M. A. Harvey, S. Baggio, M. T. Garland, R. Baggio, *Aust. J. Chem.* **2001**, *54*, 711; c) G. Webber, *Acta Crystallogr., Sect. B* **1980**, *36*, 2779; d) K. Onan, J. Rebek, T. Costello, L. Marshal, *J. Am. Chem. Soc.* **1983**, *105*, 6759; e) J. Rebek, T. Costello, L. Marshal, R. Wattle, R. C. Gadwood, *J. Am. Chem. Soc.* **1985**, *107*, 7481; f) A. M. Costero, E. Monrabal, C. Andreu, R. Martinez-Manez, J. Soto, M. Padilla-Tosta, T. Pardo, L. E. Ochano, J. M. Amigo, *J. Chem. Soc., Dalton Trans.* **2000**, 361; g) V. Y. Komarov, E. A. Ukraintseva, D. V. Soldatov, G. D. Enright, P. S. Galkin, R. Luboradzki, J. Lipkowski, *J. Inclusion Phenom. Macrocyclic Chem.* **2004**, *50*, 227; h) K. A. Byriel, K. R. Dunster, L. R. Gahan, C. H. L. Kennard, J. L. Latten, *Inorg. Chim. Acta* **1992**, *196*, 35; i) K. Kubo, N. Kato, A. Mori, H. Takeshita, *Acta Crystallogr., Sect. C* **2000**, *56*, 644; j) R. D. Rodgers, A. H. Bond, J. L. Wolf, *J. Coord. Chem.* **1993**, *29*, 187; k) L. E. Ochando, J. M. Amigo, A. M. Costero, M. Pitarch, T. Debaerdemaecker, *Cryst. Res. And Technol.* **1996**, *31*, 37; l) A. M. Costero, C. Andreu, E. Monrabal, A. Tortajada, L. E. Ochando, J. M. Amigo, *Tetrahedron* **1996**, *52*, 12499; m) A. Bashal, M. McPartlin, B. P. Murphy, H. R. Powell, S. Walker, *J. Chem. Soc., Dalton Trans.* **1994**, 1383; n) A. M. Costero, M. Pitarch, C. Andreu, L. E. Ochando, J. M. Amigo, *Tetrahedron* **1996**, *52*, 669.
- [17] R. D. Shannon, *Acta Crystallogr., Sect. A* **1976**, *32*, 751.
- [18] a) I. Bertini, C. Luchinat, *Coord. Chem. Rev.* **1996**, *150*, 1; b) J. A. Peters, J. Huskens, D. J. Raber, *J. Prog. NMR Spectrosc.* **1996**, *28*, 283.
- [19] KUMA Diffraction, *KUMA KM-4 CCD Program Package, Ver. 163*, Wrocław, Poland, **2000**.
- [20] G. M. Sheldrick, *SHELXTL Program*, Siemens Analytical X-ray Instrument Inc., Madison WI, **1991**.
- [21] G. M. Sheldrick, *SHELXL-97, Program for the Solution and Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, **1997**.

Received: September 21, 2006

Published Online: February 21, 2007