

Synthesis and structural characterisation of nickel 15-metallacrown-5 complexes with lanthanide(III) and lead(II) ions: Influence of the central metal ion size on the spin state of peripheral nickel(II) ions

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Abstract

The new 15-metallacrown-5 complexes were synthesised from nickel(II) salts and 2-picolinehydroxamic acid in the presence of lanthanide(III) (Ce, Pr, Sm, Dy, Er) or lead(II) ions. The samarium(III) and lead(II) 15-metallacrown-5 complexes were obtained as pyridine adducts and their X-ray crystal structures were determined. In the case of samarium(III) derivative, four nickel(II) ions of the metallamacrocycle are high-spin, six-coordinate and one nickel(II) ion is low-spin, square-planar. In the case of the analogous derivative of the larger lead(II), all five peripheral nickel(II) ions are six-coordinate, which results in the enlargement of cavity size of the metallacrown. The reaction of nickel 15-metallacrown-5 samarium(III) complex with copper(II) ions leads into more stable copper 15-metallacrown-5 samarium(III) complex, as shown by ¹H NMR and ESI-MS spectra.

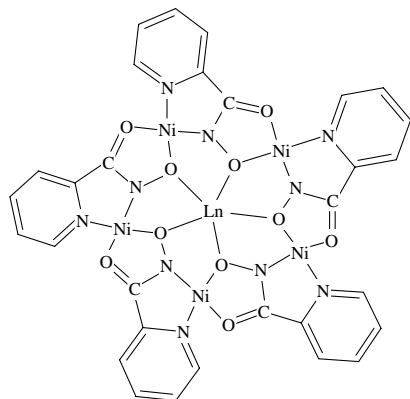
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Keywords: Metallacrowns; Lanthanide complexes; Lead complexes; Nickel complexes; Crystal structure

Heteronuclear complexes of transition metal and lanthanide ions have been intensively studied over the past decade [1]. These complexes exhibit interesting magnetic properties, and the combination of different properties of these two kinds of ions may result in novel reactivity and catalytic properties. However, selective and controlled assembly of lanthanide ions and transition metal ions into well-defined molecular structures is not an easy task. For instance, the synthesis of heteronuclear complexes containing nickel(II) and lanthanide(III) ions can be accomplished utilising organic macrocyclic ligands [1b–3]. Another strategy of assembling this type of heteronuclear complexes is based on the formation of metallamacrocyclic complexes [4]. Particularly interesting is the class of metallamacrocycles discovered by Pecoraro and co-workers, called metal-

lacrowns, that are inorganic analogues of crown ethers [5]. A combination of transition metal ions and α -aminohydroxamic acids, that form only 5-membered chelate rings, leads to pentagonal arrangement of 15-metallacrown-5 (Scheme 1). This arrangement was observed in the interesting heteropolynuclear copper(II)–lanthanide(III) and copper(II)–uranyl(VI) complexes [5–9] such as $[\text{LnCu}_5(\text{picha})_5](\text{NO}_3)_3$ and $[\text{LnCu}_5(\text{pheha})_5](\text{NO}_3)_3$, (where Ln is the lanthanide(III) ion, picha is 2-picolinehydroxamic acids dianion and pheha is (*S*)-phenylalaninehydroxamic acid dianion). These complexes containing five copper(II) ions, 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 copper 15-metallacrown-5 complexes exhibit selective recognition of anions [8a] and form enantiopure helical solids [8b]. Two analogous Nd(III) and Gd(III) derivatives containing five nickel(II) ions have also been

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Scheme 1. The general structure of $[\text{LnNi}_5(\text{picha})_5]^{3+}$ complexes.

synthesised, and characterised by mass spectrometry and magnetic moment measurements [6]. Here we report the synthesis and characterisation of new lanthanide(III) (Ce, Pr, Sm, Dy and Er) and lead(II) 15-metallacrowns-5 based on nickel(II) and 2-picolinehydroxamate, as well as X-ray crystal structures of samarium(III) and lead(II) complexes obtained as pyridine adducts.

The $[\text{LnNi}_5(\text{picha})_5](\text{NO}_3)_3$ complexes have been obtained [10] in a modified synthesis from nickel(II) nitrate in methanol using KOH as a base. The nickel 15-metallacrown-5 lead(II) complex has been synthesised [11] using nickel(II) acetate and lead(II) acetate. In the case of samarium(III) and lead(II) derivatives, diffusion of diethyl ether into pyridine solutions of these nickel 15-metallacrown-5 complexes produces crystalline pyridine adducts suitable for X-ray structural determination.

The molecular structure [12] of $[\text{SmNi}_5(\text{picha})_5(\text{py})_8(\text{NO}_3)_2](\text{NO}_3) \cdot 2(\text{py}) \cdot 2(\text{H}_2\text{O})$ complex (Fig. 1) shows 15-

metallacrown-5 core formed by five nickel(II) ions and five bridging 2-picolinehydroxamate anions, similar to that of related copper(II) complexes [6]. The central samarium(III) ion is eight-coordinate and is coordinated by five hydroxamate oxygen atoms, one bidentate nitrate anion in axial position and one monodentate axial nitrate anion at opposite side of the metallacrown. The 15-metallacrown-5 unit is only slightly buckled. Four nickel(II) ions are additionally coordinated by eight axial pyridine molecules and assume distorted octahedral geometry. The two axial pyridine molecules at each high-spin nickel(II) ion are almost parallel. The fifth nickel(II) ion is square-planar and is not bound to pyridine ligands. As expected for low-spin square-planar nickel(II), the metal–nitrogen and metal–oxygen bonds of that unique nickel(II) ion are distinctly shorter (Ni–O, 1.853 Å; Ni–N, 1.855 Å) than the respective bonds formed by four octahedral high-spin nickel(II) ions (Ni–O, 2.039 Å; Ni–N, 2.042 Å). The radius of the metallacrown cavity is 1.11 Å and matches well with the size of the eight-coordinate samarium(III) ion (1.08 Å). The cavity size of this nickel 15-metallacrown-5 is similar to that of the related copper 15-metallacrown-5 lanthanide complexes [6]. The samarium(III) ion is positioned almost exactly in the least-squares plane of the five oxygen donors of the metallacrown.

The asymmetric unit of the $[\text{PbNi}_5(\text{picha})_5(\text{py})_{11}](\text{OAc})_2 \cdot 2(\text{py}) \cdot 4\text{H}_2\text{O}$ 15-metallacrown-5 complex [12] contains the complex cation $[\text{PbNi}_5(\text{picha})_5(\text{py})_{11}]^{2+}$ (Fig. 2). The lead(II) ion is coordinated in the centre of the metallacrown by five oxygen atoms and is additionally coordinated by one axial pyridine molecule. Such a regular pentagonal–pyramidal geometry is rare for lead(II) [13,14]. The coordination of pyridine molecule in axial

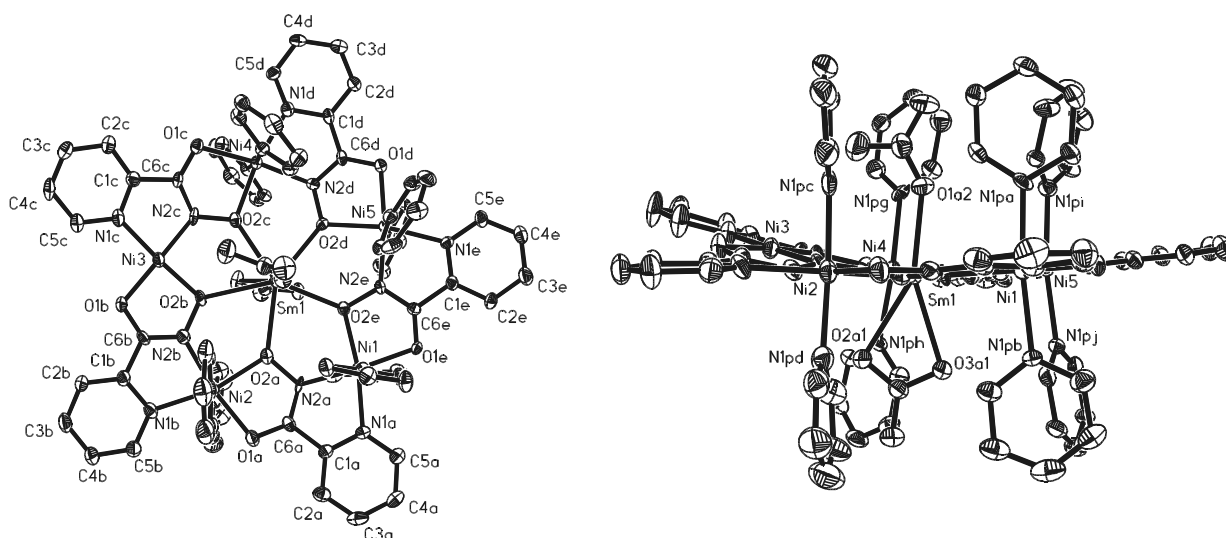


Fig. 1. Top and side view of the $[\text{SmNi}_5(\text{picha})_5(\text{py})_8(\text{NO}_3)_2]^+$ complex cation. Selected bond lengths: Sm1–O2a, 2.482(5); Sm1–O2b, 2.539(4); Sm1–O2c, 2.408(5); Sm1–O2d, 2.427(4); Sm1–O2e, 2.407(4); Sm1–O1a2, 2.348(5); Sm1–O2a1, 2.566(5); Sm1–O3a1, 2.560(5); Ni1–N1pa, 2.162(5); Ni1–N1pb, 2.174(6); Ni1–N1a, 2.072(6); Ni1–N2a, 1.994(5); Ni1–O1e, 2.021(4); Ni1–O2e, 2.027(5); Ni2–N1pc, 2.144(6); Ni2–N1pd, 2.121(7); Ni2–N1b, 2.143(6); Ni2–N2b, 1.997(6); Ni2–O1a, 2.025(5); Ni2–O2a, 2.060(4); Ni3–N1c, 1.882(6); Ni3–N2c, 1.830(6); Ni3–O1b, 1.873(5); Ni3–O2b, 1.853(5); Ni4–N1pg, 2.160(5); Ni4–N1ph, 2.155(5); Ni4–N1d, 2.076(6); Ni4–N2d, 1.994(5); Ni4–O1c, 2.031(4); Ni4–O2c, 2.035(5); Ni5–N1pi, 2.181(6); Ni5–N1pj, 2.134(5); Ni5–N1e, 2.107(5); Ni5–N2e, 1.991(5); Ni5–O1d, 2.038(4); Ni5–O2d, 2.049(4) Å.

position reflects the soft character of lead(II) ion in comparison with the harder and more oxophilic lanthanide(III) ions, which prefer coordination of two nitrate anions in $[\text{SmNi}_5(\text{picha})_5(\text{py})_8(\text{NO}_3)_2]^+$. The coordination of the lead(II) ion is hemi-directed and the ion is slightly displaced by 0.233(1) Å from the mean plane formed by five hydroxamate oxygen atoms in a direction opposite to the bound pyridine ligand. This effect reflects the influence of the stereochemically active lone pair of electrons of lead(II) [15]. As a result of this displacement towards the open face, the lead(II) ion adopts umbrella-like structure [13,14]. The main difference between $[\text{SmNi}_5(\text{picha})_5(\text{py})_8(\text{NO}_3)_2]^+$ and $[\text{PbNi}_5(\text{picha})_5(\text{py})_{11}]^{2+}$ is that in the latter complex, all five nickel(II) ions bind two axial pyridine molecules and are high-spin octahedral. This results in the expansion of the cavity of the nickel 15-metallacrown-5. Thus the cavity radius is 1.21 Å and matches well with the radius of the six-coordinate lead(II) ion (1.19 Å). In this way, the radius of the central ion influences the spin-state of the nickel(II) ions; for the larger lead(II) ion all five nickel(II) ions are high-spin to obtain maximum metallamacrocycle size, while for the smaller samarium(III) ion the optimal cavity size corresponds to a combination of four high-spin nickel(II) ions and one low-spin nickel(II) ion. In the $[\text{PbNi}_5(\text{picha})_5(\text{py})_{11}]^{2+}$ complex, steric interaction of the six pyridine molecules coordinated on one side of the metallamacrocycle results in a slight expansion of this face of the complex. This interaction is manifested in buckling of the metallamacrocycle core, nonparallel arrangement of the pyridine molecules coordinated to the same nickel(II) ion and cone-like arrangement of the 10 pyridine molecules coordinated to the nickel(II) ions. The $[\text{PbNi}_5(\text{picha})_5(\text{py})_{11}]^{2+}$ complex cation is present also in the structure of the related $[\text{PbNi}_5(\text{picha})_5(\text{py})_{11}](\text{NO}_3)_2 \cdot 2(\text{py})$ complex obtained from the nickel(II) nitrate. Although the X-ray crystal structure of this compound ($a = 15.872$

(3), $b = 22.691(4)$, $c = 27.004(4)$ Å, $V = 9668(3)$ Å³) could not be satisfactorily solved, it clearly shows the coordination of two pyridine molecules to each nickel(II) ion.

The $[\text{PbNi}_5(\text{picha})_5(\text{py})_{11}](\text{OAc})_2 \cdot 2(\text{py}) \cdot 4\text{H}_2\text{O}$ complex loses solvent molecules upon drying and converts into $[\text{PbNi}_5(\text{picha})_5(\text{py})_6](\text{OAc})_2$. The pyridine molecules are further dissociated in diluted methanol solution, as shown by ESI MS spectra which show molecular peaks corresponding to $[\text{PbNi}_5(\text{picha})_5](\text{OAc})^+$ and $[\text{PbNi}_5(\text{picha})_5]^{2+}$. The ¹H NMR spectrum (Supplementary Fig. 1) of the solution of $[\text{PbNi}_5(\text{picha})_5(\text{py})_6](\text{OAc})_2$ in deuterated pyridine exhibits only one set of paramagnetically shifted 2-picolinehydroxamate signals consistent with the structure of nickel 15-metallacrown-5 (two of the signals are overlapped, as confirmed by integration).

One set of ligand signals is observed also for the DMSO-*d*₆ solutions of the $[\text{LnNi}_5(\text{picha})_5](\text{NO}_3)_3$ complexes (Supplementary Fig. 1). The spectral pattern of the 2-picolinehydroxamate is similar to that observed in the related copper(II) metallacrowns [6,16] that indicate a dominant contact contribution to the paramagnetic shift and a similar mechanism of spin delocalization. The ESI MS spectra of the $[\text{LnNi}_5(\text{picha})_5](\text{NO}_3)_3$ complexes in methanol show $[\text{LnNi}_5(\text{picha})_5](\text{NO}_3)_2^+$ and $[\text{LnNi}_5(\text{picha})_5](\text{NO}_3)^{2+}$ molecular ions (Supplementary Fig. 2) corresponding to the intact nickel 15-metallacrown-5.

¹H NMR spectroscopy was used to compare the relative stability of nickel 15-metallacrown-5 lanthanide(III) complexes with copper 15-metallacrown-5 lanthanide(III) complexes. The spectra of the latter complexes measured for DMSO-*d*₆ solutions in the presence of excess of nickel(II) ions do not change over a period of 3 weeks, indicating no exchange of copper(II) for nickel(II). On the other hand, the ¹H NMR spectra of DMSO-*d*₆ solutions of $[\text{SmNi}_5(\text{picha})_5](\text{NO}_3)_3 \cdot 10\text{H}_2\text{O}$ combined with 3, 5 or 10 equiv. of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ change in time. The final

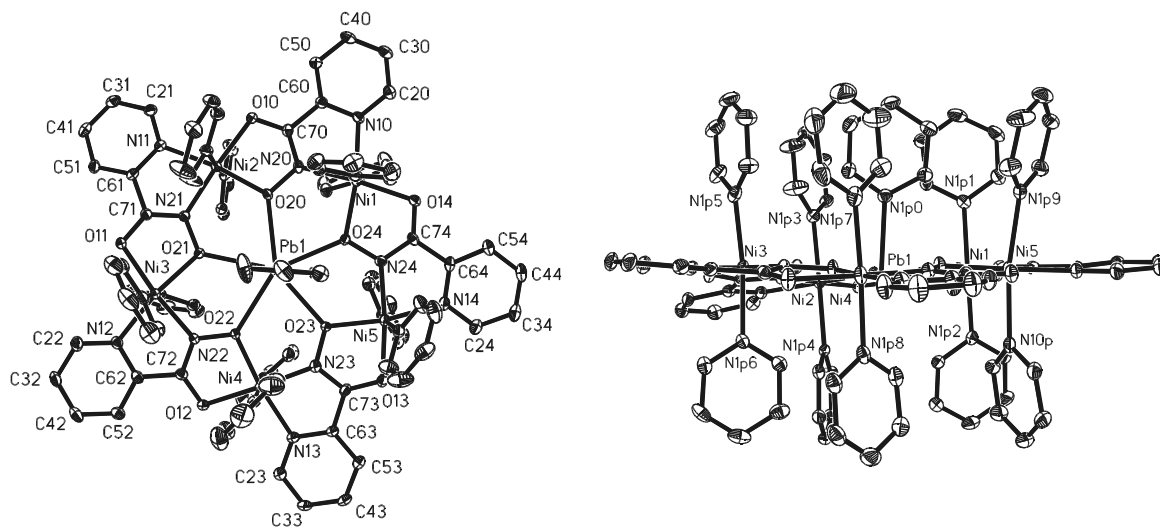


Fig. 2. Top and side view of the $[\text{PbNi}_5(\text{picha})_5(\text{py})_{11}]^{2+}$ complex cation. Selected bond lengths: Pb1–N1p0, 2.414(3); Pb1–O21, 2.548(3); Pb1–O22, 2.572(3); Pb1–O23, 2.577(3); Pb1–O24, 2.558(3) Å.

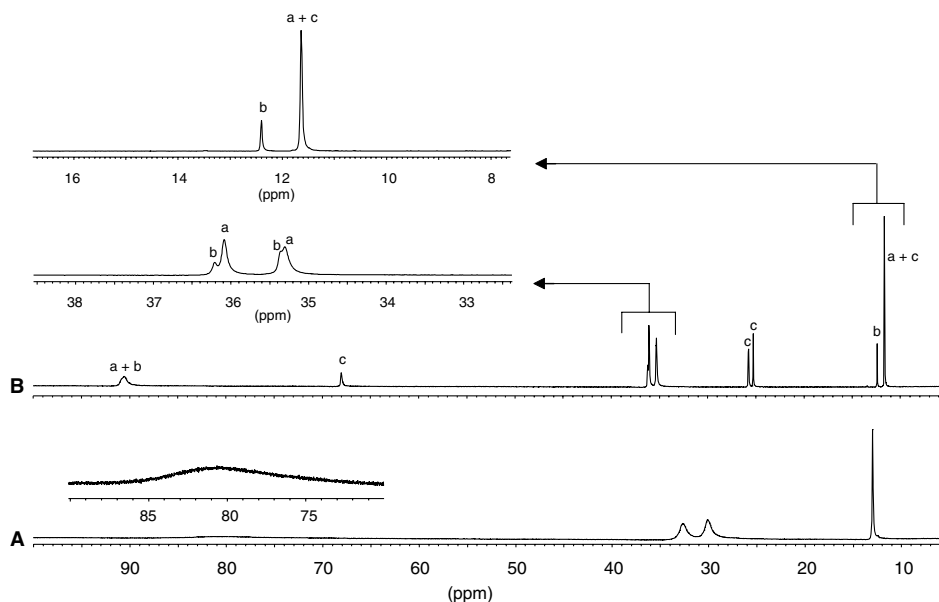


Fig. 3. ^1H NMR spectra ($\text{DMSO-}d_6$, 298 K) of $[\text{SmNi}_5(\text{picha})_5](\text{NO}_3)_3 \cdot 10\text{H}_2\text{O}$ complex (trace A), $[\text{SmNi}_5(\text{picha})_5](\text{NO}_3)_3 \cdot 10\text{H}_2\text{O}$ reacted for one month with 5 equiv. of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (trace B), 'a' refer to signals of $[\text{SmCu}_5(\text{picha})_5](\text{NO}_3)_3$ complex, 'b' refer to signals of $[\text{Cu}_5(\text{picha})_4](\text{NO}_3)_2$ complex, 'c' refer to signals of $[\text{NiCu}_4(\text{picha})_4](\text{NO}_3)_2$ complex.

spectra (Fig. 3, Supplementary Fig. 3) recorded after one month show that the starting nickel 15-metallacrown-5 complex $[\text{SmNi}_5(\text{picha})_5]^{3+}$ was converted into copper 15-metallacrown-5 complex $[\text{SmCu}_5(\text{picha})_5]^{3+}$. Additionally, signals of the 12-metallacrown-4 $[\text{Cu}_5(\text{picha})_4]^{2+}$ [16] were observed as well as those of $[\text{NiCu}_4(\text{picha})_4]^{2+}$, which is formed in a further reaction of $[\text{Cu}_5(\text{picha})_4]^{2+}$ with nickel(II) ions [16]. The presence of $[\text{SmCu}_5(\text{picha})_5]^{3+}$, $[\text{Cu}_5(\text{picha})_4]^{2+}$ and $[\text{NiCu}_4(\text{picha})_4]^{2+}$ species in the final solution is also confirmed by ESI-MS spectra (Supplementary Fig. 4). The ^1H NMR spectra of these samples recorded after 1, 2, 8, 22 and 30 days are very complicated and indicate the presence of many intermediates, possibly of the $[\text{SmNi}_x\text{Cu}_{5-x}(\text{picha})_5]^{3+}$ type (Supplementary Figs. 5 and 6).

In conclusion, the nickel 15-metallacrown-5 complexes have been characterised for the first time by X-ray crystallographic methods. The 15-metallacrown-5 unit can adjust itself into the geometric requirements of the central ion by changing the spin state of the peripheral nickel(II) ions. The nickel 15-metallacrown-5 system is also well preserved in solution, although the described complexes are less stable than the corresponding copper 15-metallacrown-5 derivatives.

Appendix A. Supplementary data

Supplementary data for the structures of $[\text{SmNi}_5(\text{picha})_5(\text{py})_8(\text{NO}_3)_2](\text{NO}_3) \cdot 2(\text{py}) \cdot 2(\text{H}_2\text{O})$ and $[\text{PbNi}_5(\text{picha})_5(\text{py})_{11}](\text{OAc})_2 \cdot 2(\text{py}) \cdot 4\text{H}_2\text{O}$ complexes are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.uk, quoting the deposi-

tion numbers CCDC 298733 and CCDC 298732, respectively. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.04.026.

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- [10] Synthesis of $[\text{SmNi}_5(\text{picha})_5](\text{NO}_3)_3 \cdot 10\text{H}_2\text{O}$ and crystallisation of $[\text{SmNi}_5(\text{picha})_5(\text{py})_8(\text{NO}_3)_2](\text{NO}_3) \cdot 2(\text{py}) \cdot 2(\text{H}_2\text{O})$: 2-picolinehydrox-

amic acid [6] (0.165 g, 1.19 mmol) was added to a stirred solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.346 g, 1.19 mmol) in methanol (20 ml) for 10 min. A solution of KOH (0.134 g, 2.39 mmol) in methanol (10 ml) was added dropwise under stirring, causing colour change from light green to dark red. $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.105 g, 0.238 mmol) was added and a yellow green precipitate started to appear after about 30 min. The mixture was stirred overnight and the obtained precipitate was filtered, washed with water, methanol and air-dried. Yield: 42%. Elemental Anal.: Calc. for $\text{SmNi}_5\text{C}_{30}\text{H}_{40}\text{N}_{13}\text{O}_{29}$: C, 24.17, H, 2.70, N, 12.22. Found C, 23.80, H, 2.48, N, 11.89%. ^1H NMR (DMSO- d_6): δ 12.97, 30.10, 32.70 and 82.03 ppm. ESI-MS(+) gave $[\text{M}]^+$ of 1248 m/z , $[\text{M}]^{2+}$ of 593 m/z in methanol. Diethyl ether was allowed to diffuse into pyridine solution containing $[\text{SmNi}_5(\text{picha})_5(\text{NO}_3)_3 \cdot 10\text{H}_2\text{O}]$. After ten days deep reddish crystals of $[\text{SmNi}_5(\text{picha})_5(\text{py})_8(\text{NO}_3)_2](\text{NO}_3) \cdot 2(\text{py}) \cdot 2(\text{H}_2\text{O})$ suitable for X-ray measurement were formed. The crystals lose the solvent molecules and quickly decompose in air.

The other $[\text{LnNi}_5(\text{picha})_5](\text{NO}_3)_3$ complexes (Ln = Ce, Pr, Dy and Er) have been prepared in the same way as $[\text{SmNi}_5(\text{picha})_5](\text{NO}_3)_3 \cdot 10\text{H}_2\text{O}$ complex in 42%, 43%, 40% and 30% yields, respectively. $[\text{CeNi}_5(\text{picha})_5](\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$: Elemental Anal. Calc. for $\text{CeNi}_5\text{C}_{30}\text{H}_{38}\text{N}_{13}\text{O}_{28}$ (MW = 1462): C, 24.64, H, 2.62, N, 12.45. Found C, 24.41, H, 2.40, N, 12.22%. ^1H NMR (DMSO- d_6 , ppm): δ 12.82, 29.81, 32.11 and 81.44 ppm. ESI-MS(+) gave $[\text{M}]^+$ of 1233 m/z , $[\text{M}]^{2+}$ of 586 m/z in methanol/acetic acid mixture. $[\text{PrNi}_5(\text{picha})_5](\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$: Elemental Anal. Calc. for $\text{PrNi}_5\text{C}_{30}\text{H}_{38}\text{N}_{13}\text{O}_{28}$ (MW = 1463): C, 24.63, H, 2.62, N, 12.45. Found C, 24.78, H, 2.49, N, 12.44%. ^1H NMR (DMSO- d_6 , ppm): δ 12.14, 28.96, 30.84 and 79.69 ppm. ESI-MS(+) gave $[\text{M}]^+$ of 1236 m/z , $[\text{M}]^{2+}$ of 588 m/z in methanol/acetic acid mixture. $[\text{DyNi}_5(\text{picha})_5](\text{NO}_3)_3 \cdot 8\text{H}_2\text{O}$: Elemental Anal. Calc. for $\text{DyNi}_5\text{C}_{30}\text{H}_{36}\text{N}_{13}\text{O}_{27}$ (MW = 1467): C, 24.56, H, 2.47, N, 12.42. Found C, 24.60, H, 1.93, N, 12.00%. ^1H NMR (CD_3OD , ppm): δ 16.18, 32.19, 39.30 and very broad band around 80 ppm. ESI-MS(+) gave $[\text{M}]^+$ of 1259 m/z , $[\text{M}]^{2+}$ of 599 m/z in methanol/acetic acid mixture. $[\text{ErNi}_5(\text{picha})_5](\text{NO}_3)_3 \cdot 11\text{H}_2\text{O}$: Elemental Anal. Calc. for $\text{ErNi}_5\text{C}_{30}\text{H}_{40}\text{N}_{13}\text{O}_{29}$ (MW = 1525): C, 23.62, H, 2.78, N, 11.94. Found C, 23.28, H, 2.96, N, 11.46%. ^1H NMR (DMSO- d_6 , ppm): δ 12.98, 29.80, 31.83 and 81 ppm. ESI-MS(+) gave $[\text{M}]^+$ of 1265 m/z , $[\text{M}]^{2+}$ of 601 m/z in methanol/acetic acid mixture. The ^1H NMR spectra were collected on Bruker AMX 500 spectrometer. The positive mode ESI-MS spectra of methanol solutions were measured on Finnigan MAT TSQ 700 triple stage quadrupole mass spectrometer and on Micromass LCT (TOF) instrument. The elemental analyses were carried out on a Perkin–Elmer 2400 CHN elemental analyzer.

[11] Preparation of $[\text{PbNi}_5(\text{picha})_5(\text{py})_6](\text{OAc})_2$: 2-picolinedihydroxamic acid (0.083 g, 0.60 mmol) was added to a stirred solution of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.148 g, 0.60 mmol) in methanol (25 ml), causing colour change from pale green to brown–red. The resultant solution

was stirred for 15 min, solid $\text{Pb}(\text{CH}_3\text{COO})_2$ (0.045 g, 0.12 mmol) was added and the solution was left to stir overnight. The mixture was evaporated to dryness and the residue dissolved in pyridine. A slow diffusion of diethyl ether into the pyridine solution results in the formation of deep dark red crystals of $[\text{PbNi}_5(\text{picha})_5(\text{py})_{11}](\text{OAc})_2 \cdot 2(\text{py}) \cdot 4\text{H}_2\text{O}$ suitable for X-ray measurement. This crystalline product was dried under vacuum for 1 day to give $[\text{PbNi}_5(\text{picha})_5(\text{py})_6](\text{OAc})_2$ complex in 37% overall yield. Elemental Anal. Calc. for $\text{PbNi}_5\text{C}_{64}\text{H}_{56}\text{N}_{16}\text{O}_{14}$ (MW = 1774): C, 43.33, H, 3.18, N, 12.63. Found C, 43.53, H, 3.47, N, 12.38%. ^1H NMR (pyridine- d_5 , ppm): δ 13.96, 37.72 and a very broad signal around 102 ppm. ESI-MS(+) gave $[\text{M}]^+$ of 1240 m/z , $[\text{M}]^{2+}$ of 590 m/z in pyridine/methanol mixture.

- [12] Crystallographic data: Data were collected on a KUMA KM-4 with area CCD detector using $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) (KUMA KM-4 CCD Software, Version 171.1, KUMA DIFFRACTION, Wrocław, 2002). Face-indexed analytical absorption was performed using SHELXTL program (G.M. Sheldrick, Acta Crystallogr. A 46 (1990) 467). Structures were resolved by direct methods using SHELXS-97 and refined using SHELXL-97 (G.M. Sheldrick, SHELXL-97, Program for the Solution and Refinement of Crystal Structures, Universität Göttingen, Göttingen, Germany, 1997). Crystal Data for Sm-complex: $(\text{C}_{70}\text{H}_{60}\text{N}_{20}\text{O}_{16}\text{Ni}_5\text{Sm})\text{NO}_3 \cdot 2(\text{C}_5\text{H}_5\text{N}) \cdot 2(\text{H}_2\text{O})$, Mr = 2138.52, triclinic, space group $P\bar{1}$ (no. 2), $a = 12.278(3)$, $b = 28.753(5)$, $c = 29.379(5) \text{ \AA}$, $\alpha = 70.02(2)$, $\beta = 84.57(2)$, $\gamma = 78.22(2)^\circ$, $V = 9539(3) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.486 \text{ g cm}^{-3}$, $\rho_{\text{obs}} = 1.48 \text{ g cm}^{-3}$ (by flotation); $2.91^\circ \leq \theta \leq 27^\circ$; crystal dimensions, $0.32 \times 0.21 \times 0.18 \text{ mm}^3$; $\mu = 1.650 \text{ mm}^{-1}$; $T = 100(2) \text{ K}$; 55924 measured reflections; 40875 independent reflections, $R_{\text{int}} = 0.0565$; 23059 observed reflections ($>2\sigma(\text{I})$); 2341 parameters; $R_1 = 0.0731$, $wR_2 = 0.1785$ for all reflections, residual electron density on final $\Delta\rho$ map: +1.459 and $-1.509 \text{ e \AA}^{-3}$. Crystal Data for Pb-complex: $(\text{C}_{85}\text{H}_{75}\text{N}_{21}\text{O}_{10}\text{Ni}_5\text{Pb}) \cdot 2(\text{C}_5\text{H}_5\text{N}) \cdot 4(\text{H}_2\text{O})$, Mr = 2399.75, monoclinic, space group $P2_1/c$ (no. 14), $a = 16.096(3)$, $b = 23.691(5)$, $c = 26.786(5) \text{ \AA}$, $\beta = 97.99(3)^\circ$, $V = 10115(3) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.576 \text{ g cm}^{-3}$, $\rho_{\text{obs}} = 1.57 \text{ g cm}^{-3}$ (by flotation), $2.88^\circ \leq \theta \leq 28.52^\circ$, crystal dimensions, $0.31 \times 0.16 \times 0.13 \text{ mm}^3$; $\mu = 2.649 \text{ mm}^{-1}$; $T = 100(2) \text{ K}$; 135262 measured reflections, 24107 independent reflections, $R_{\text{int}} = 0.0480$, 19779 observed reflections ($>2\sigma(\text{I})$), 1341 parameters, $R_1 = 0.0447$, $wR_2 = 0.1010$ for all reflections, residual electron density on final $\Delta\rho$ map: +1.374 and $-0.867 \text{ e \AA}^{-3}$.
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