



Ion recognition properties of new pyridine-2,6-dicarboxamide bearing propeller-like pendant residues: multi-spectroscopic approach

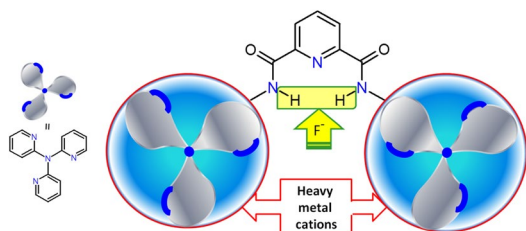
Ewa Wagner-Wysiecka¹ · Natalia Łukasik¹ · Andrzej Okuniewski² · Błażej Galiński¹

Received: 5 June 2019 / Accepted: 10 February 2020 / Published online: 12 March 2020
© The Author(s) 2020

Abstract

The synthesis and ion binding properties of new amide derived from propeller-like tris(2-pyridyl)amine and 2,6-pyridine-dicarboxylic acid chloride were described. Amide binds divalent metal cations: copper(II), nickel(II), zinc(II), and lead(II) in acetonitrile. In acetonitrile:water mixture (9:1 v/v) amide interacts only with copper(II) and nickel(II) cations forming complexes of 1:1 stoichiometry. It was found that the introduction of bulky, nitrogen donor atom bearing pendant groups can influence coordination mode of pyridine-2,6-dicarboxamides. The probable model of ligand-ion interactions is proposed on the basis of ¹H NMR and FT-IR spectroscopy.

Graphic abstract



Keywords Supramolecular chemistry · Heterocycles · Synthesis · Spectroscopy

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s00706-020-02558-w>) contains supplementary material, which is available to authorized users.

✉ Ewa Wagner-Wysiecka
ewa.wagner-wysiecka@pg.edu.pl

✉ Natalia Łukasik
natalia.lukasik@pg.edu.pl

¹ Department of Chemistry and Technology of Functional Materials, Faculty of Chemistry, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland

² Department of Inorganic Chemistry, Faculty of Chemistry, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland

Introduction

Among many aspects of supramolecular chemistry, the design and synthesis of compounds capable of ion recognition is still one of the most intensively studied areas. An interesting building block in molecular receptor design seems to be tris(2-pyridyl)amine reported for the first time by Wibaut et al. [1]. Complexes of tris(2-pyridyl)methane or tris(2-pyridyl)phosphine with transition metal cations were studied exhaustively by McWhinnie [2–6]. Tris(2-pyridyl)amine residue can act both as a bidentate or tridentate ligand [7] forming mostly six-membered chelate rings in complexes with transition metal cations with little distortion from an ideal octahedral geometry [8]. Complexes of tris(2-pyridyl)amine with Re, Ir, and W synthesized by Crabtree [9] were proposed as thermally stable, potential catalysts even though the catalytic activity neither in reactions of alkanes dehydrogenation nor in dihydroxylation of alkenes was found. Yang

et al. [10] described a bidentate, blue luminescent complex of tris(2-pyridyl)amine with zinc(II) in tetrahydrofuran and solid state. Copper(I) complex was effectively applied as a catalyst in carbene and nitrene transfer reactions [11], whereas complexes with iron(II) and cobalt(II) were used in catalytic ethylene polymerization [12].

Another important group of molecular receptors constitute pyridine-2,6-dicarboxamides (dipicolinic acid amides) [13] showing among others affinity towards *d* and *f* block metal cations [14] and uranyl cations [15]. Wagner-Wysiecka et al. [16] described naphthyl- and anthrylpyridine-2,6-dicarboxamides for spectrophotometric and spectrofluorimetric recognition of copper(II) and lead(II) in acetonitrile. Complexes of dipicolinic acid derivatives with chromium(III) and manganese(III) ions were tested as catalysts in alkene epoxidation and hydroxylation reactions [17]. It was reported that copper(II) complexes of dipicolinic acid amides can also show cytotoxic activity [18, 19].

Pyridine-2,6-dicarboxamides due to the presence of NH groups can also act as anion receptors [20–26]. Derivatives of dipicolinic acid bearing *N*-substituted quinoline moieties were proposed for spectrofluorimetric determination of chloride, acetate, and pyrophosphate anions in aqueous solutions [27, 28]. Sessler et al. [29] reported the synthesis and transport ability of calix [4] pyrrole derivative of dipicolinic acid complexing chloride anion inside the macrocycle in aqueous solutions.

Taking all above into consideration we decided to join two interesting building blocks: tris(2-pyridyl)amine and pyridine-2,6-dicarboxamide into one molecule **1** (Scheme) and investigate the influence of bulky pendant N-donor residues on its ion binding properties.

We are convinced that the obtainment of a new ligand **1** and characterization of its complexation properties may be useful for many branches where molecular receptors find application e.g. in sensor technology [30, 31], biomedical applications [32, 33], catalysis [34, 35], separation processes [36, 37], and many others.

Results and discussion

Synthesis

Amide **1** to the best of our knowledge (according to Chemical Abstracts) has not been described in the literature so far. The amide was prepared in a very simple, well proved synthetic procedure [16, 26, 38] using 2,6-pyridinecarboxylic acid dichloride and 5-amino-2,2',2''-tris-2-pyridylamine in the presence of triethylamine as a base in DMF (Scheme 1). The pure compound was obtained with satisfactory yield i.e. 70% after crystallization from propan-2-ol. The compound was fully characterized by ¹H NMR, ¹³C NMR, FT-IR, and

HR-MS. Assignment of signals to groups of protons in ¹H NMR spectrum was based on two-dimensional (COSY) spectrum.

Ligand–metal cation complexation studies

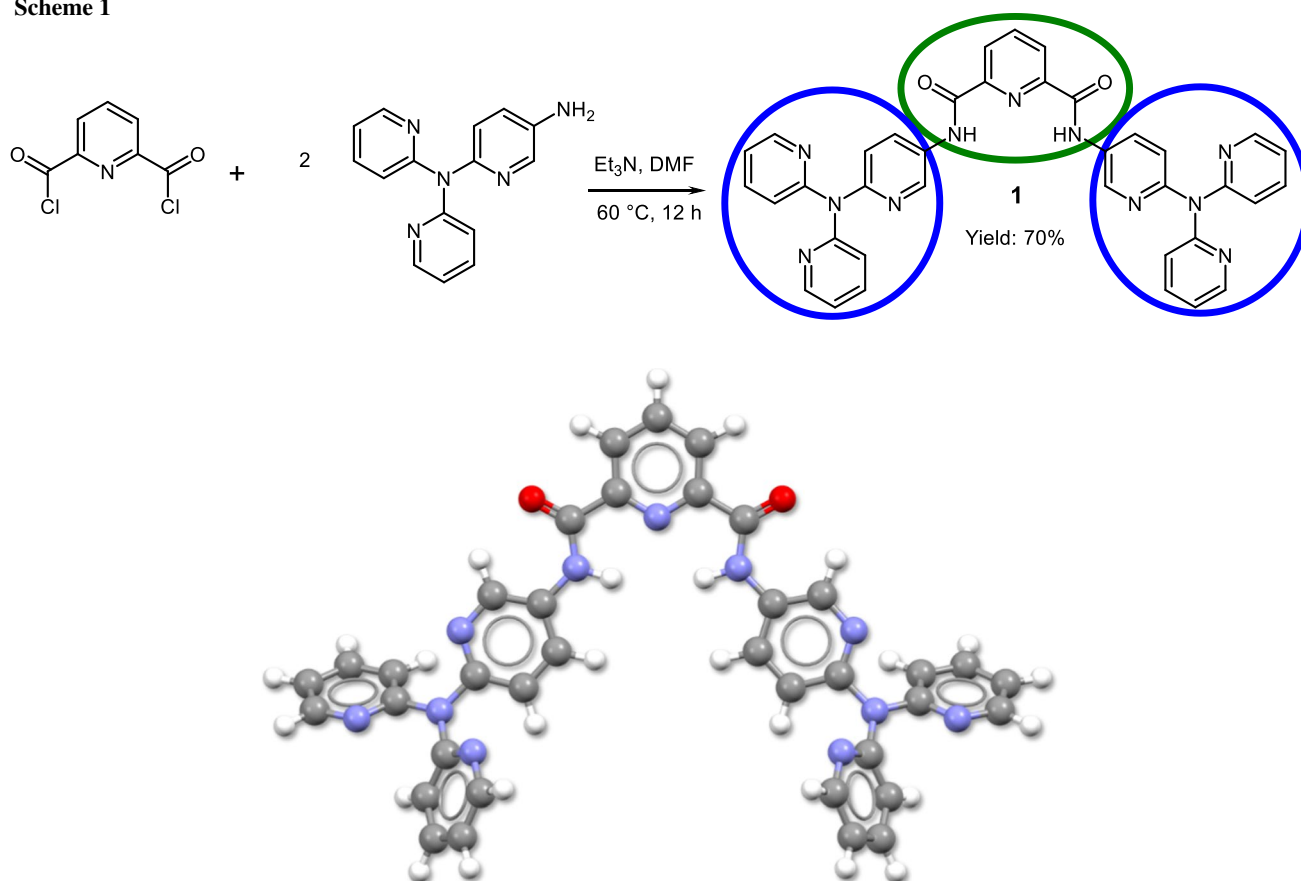
The geometry of **1** (Scheme 1, bottom) was optimized with Gaussian 09 W rev. D.01 [39] at the B3LYP/6-31G(d,p) level of theory with D3 dispersion correction by Grimme. The starting structure of **1** was hand-drawn in GaussView 5.0.9 [23] based on similar structures deposited to CSD [41]. After optimization, vibrational frequencies were calculated at the same level of theory. The analysis shows that there are no negative frequencies, so the optimized structure is, in fact, in a local minimum of the potential energy surface. Calculated IR spectrum is presented in FigESM.15. The optimized molecule has a mirror plane passing through it (*C_s* point group). The central diamide part is flattened and coplanar with adjacent pyridine fragments. Tertiary N-atoms adopt almost planar geometry with the distance of N-atom from the plane defined by three bonded C-atoms of ca. 0.064 Å. Pyridine fragments attached to tertiary N-atom form propeller-like shape with dihedral angles between aromatic rings of about 60°.

1 comprises two possible coordination centers. The first one is amide residue (green circle, Scheme 1) with two nitrogen donor atoms from amide groups and one pyridine nitrogen atom. Metal cations can also be coordinated via oxygen atoms of an amide moiety [42]. The two tris-pyridylamine residues (blue circles, Scheme 1) introduce together eight nitrogen atoms, however, not all of them must act as donor atoms in metal cation complex formation [43–45]. The proposed model of ligand suggests that pendant pyridine moieties seem to be more accessible as complexation center (larger molecular cavity) than a central pyridine atom with neighboring amide nitrogen donor atoms.

UV–Vis spectral studies

Metal cation complexation studies by UV–Vis spectroscopy have shown no spectral changes in the presence of alkali, alkaline earth, and heavy metal perchlorates in aprotic highly dipolar DMSO. In acetonitrile—protic dipolar solvent—spectral changes upon titration of **1** were observed in the presence of divalent heavy metal cations of *d*-block: nickel(II), zinc(II), and copper(II). Spectral response was also found upon titration with lead(II) perchlorate. Electronic spectrum of **1** in acetonitrile exhibits bands at 201, 268, and 305 nm which can be assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The presence of metal salts causes a small blue shift and hypochromic effect observable in the region of 290–380 nm. In all cases these changes are accompanied by the small increase of the intensity

Scheme 1



and broadening of a band in the region of higher energy at $\sim 230\text{ nm}$ (FigESM.5). Electronic spectra suggest the formation of the nitrogen-bonded metal complexes [46].

Stability constant values of the complexes were estimated on the basis of UV–Vis titration experiments carried out in acetonitrile at constant ionic strength ($10^{-2}\text{ mol/dm}^3\text{ TBAClO}_4$). Changes upon titration of **1** with metal perchlorates are shown in Fig. 1a–d.

Titration with lead(II) perchlorate results in titration trace with well pronounced isosbestic point at $\sim 300\text{ nm}$ indicating one equilibrium (Fig. 1a). New absorption maximum appears at 295 nm . Molar ratio plot in this case suggests that lead(II) can form complexes of Pb_2L type (FigESI.6c) with calculated, from titration experiments, the stability constant value ($\log K$) 9.8 ± 0.3 (Table 1).

Upon titration with zinc(II) and nickel(II) salts similar, but not identical trend of spectral changes was observed within titration experiment i.e. the decrease of the intensity of band at $\sim 325\text{ nm}$ and its slight hypsochromic shift (Fig. 1b, c). Molar ratio plots (FigESI.6.a and b) point out that in the presence of nickel(II) and zinc(II) cations systems equilibrate at approx. equimolar amount of the ligand and salts, suggesting the formation of ML type complexes under the measurement conditions. Stability

constant values ($\log K$) of 1:1 complexes of **1** are presented in Table 1.

Slightly different results were obtained upon titration with copper(II) perchlorate (Fig. 1d). At the beginning of titration, the decrease of the main absorption band is observed, similarly as for zinc(II) and nickel(II). At higher copper(II) salt concentration the change of titration trace is noticed. It may indicate, the existence of more than one complex under experiment conditions or/and the change of the coordination mode of copper(II) cation at higher excess of metal salt. However, both molar ratio plot (FigESI.6d) and fit of experimental data in OPIUM software [47] suggest the formation of 1:1 complex. Thus, to confirm or exclude the hypothesis of change of coordination mode, a series of spectra in the presence of copper(II) salt was registered at higher concentration than it was used in titration experiments described above, to trace $d-d$ transition bands (FigESM.7). In acetonitrile copper(II) exists as solvato-complex $[\text{Cu}(\text{MeCN})_6]^{2+}$ with weak and broad $d-d$ transition band at 780 nm [48] what corresponds to distorted octahedral geometry of complex. In our case for used salt $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ this band is observed at 765 nm . The electronic spectrum of **1** registered at higher concentrations shows no absorption bands in Vis–NIR ($400\text{--}900\text{ nm}$) region. In the presence of equimolar

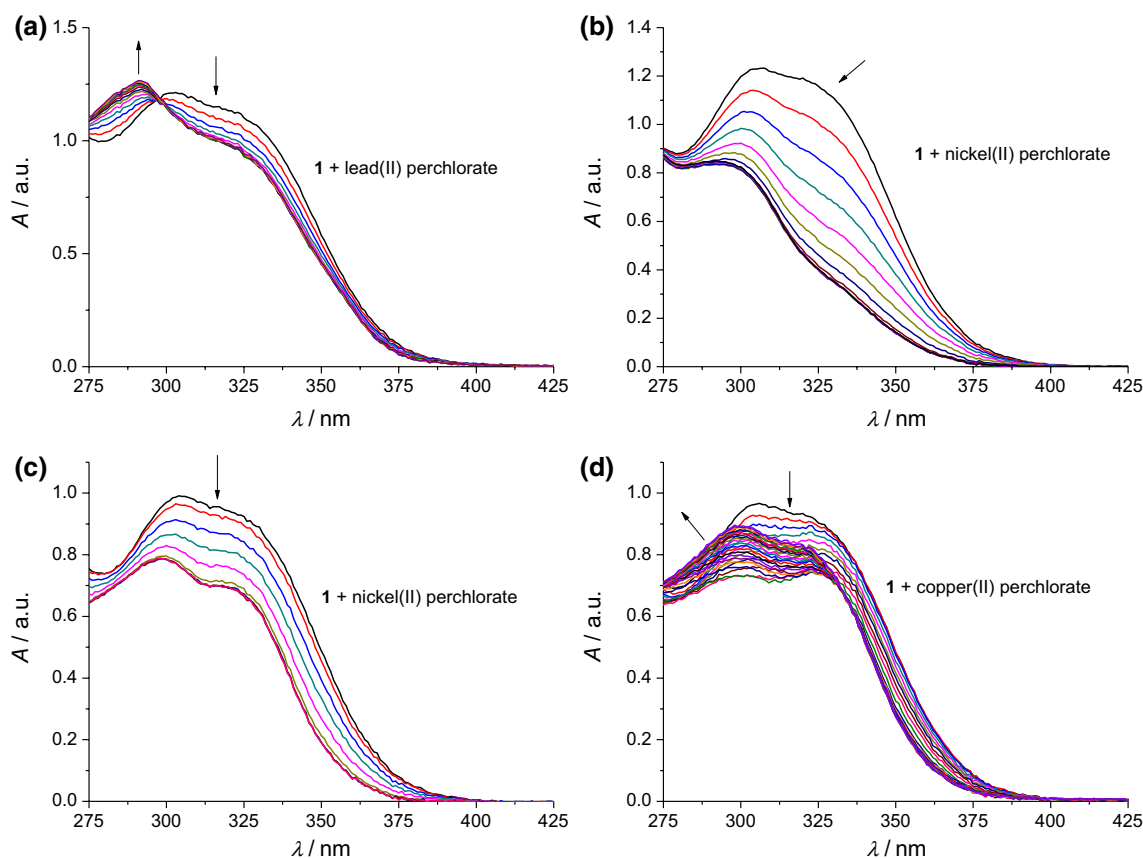


Fig. 1 Changes in UV-Vis spectra (275–425 nm) of ligand **1** solution upon titration with: **a** lead(II) perchlorate ($0 \leq R \leq 5.93$; $c_1 = 3.19 \times 10^{-5}$ mol/dm³); **b** nickel(II) perchlorate ($0 \leq R \leq 2.89$; $c_1 = 3.19 \times 10^{-5}$ mol/dm³); **c** zinc(II) perchlorate ($0 \leq R \leq 1.54$;

$c_1 = 2.55 \times 10^{-5}$ mol/dm³); **d** copper(II) perchlorate ($0 \leq R \leq 2.79$; $c_1 = 2.55 \times 10^{-5}$ mol/dm³) in acetonitrile at ionic strength 10^{-2} mol/dm³ (TBA perchlorate), R salt to ligand

Table 1 Stability constant values ($\log K$) of complexes of **1** with metal perchlorates in acetonitrile and acetonitrile:water (9:1, v/v) solvent system (at constant ionic strength, 10^{-2} mol/dm³ TBAClO₄)

Solvent	Complex stoichiometry and stability constant values			
Acetonitrile	1·Pb₂	1·Zn	1·Ni	1·Cu
	9.8 ± 0.3	7.1 ± 0.3	6.4 ± 0.4	6.0 ± 0.1
Acetonitrile:water (9:1, v,v)	No significant spectral changes			
			1·Ni	1·Cu
			4.60 ± 0.04	5.51 ± 0.04

amount of copper(II) perchlorate, two bands at ~450 and 600 nm are seen and upon addition of twofold excess of copper(II) salt, these bands shift slightly towards the spectral region of lower energy. At threefold excess of copper perchlorate the bands appear at 460 and 650 nm. The peak at 450 nm can be ascribed as metal to ligand charge transfer (MLCT) band. A band at ~600 nm arises due to $d-d$ transitions and can suggest square-planar copper(II) complex [49]. The shift towards higher wavelength values can be a result of change of the geometry to a distorted square planar or tetrahedral conformation [50]. On the basis of all above

we assumed that under titration conditions 1:1 complex of **1** with copper(II) of stability constant value $\log K 6.0 \pm 0.1$ is dominating. Stability constant values of complexes of **1** with metal perchlorates are summarized in Table 1.

Comparing some available reference data of stability constant values of complexes of pyridine-2,6-dicarboxamides in acetonitrile [16, 51] (compounds **2-6** shown in FigESM.8) the effect of the introduction of additional coordination centers as two, bulky pendant tris-2-pyridylamine residues is quite well seen. As described in literature, metal cations complexation can be connected with bathochromic shift and/

or hyperchromic effect in absorption spectra as a result of the engagement of pyridine-2,6-dicarboxamide amide residue in metal cation coordination via nitrogen atoms of an amide residue and a pyridine ring. The complex formation by **1** in acetonitrile is associated with hypochromic effect and a noticeable hypsochromic shift of the absorption band suggesting different mode of metal cation coordination. The stability constant value obtained for the complex of **1** with lead(II) is slightly higher than for 2:1 (M:L) complexes of this cation with β -substituted naphthyl- and anthryl- analogs (compounds **2** and **3**, FigESM8) described by us earlier (log K : 9.8 ± 0.3 vs. 9.02 ± 0.05 and 9.40 ± 0.22 , respectively) [16]. As proposed in previous studies, lead(II) cations are coordinated by oxygen atoms of naphthyl- and anthrylpyridine-2,6-dicarboxamides (both experiments were carried out in acetonitrile). The observed difference in binding constant values can be probably a result of a steric hindrance of bulky pendant arms of **1** in the complexation of relatively large (ionic radii 119 pm) lead(II) cation or a result of different coordination mode or both these factors. In the case of copper(II), zinc(II), and nickel(II) 1:1 complexes of **1** the stability constant values are higher than those described for α -substituted naphthalene and anthracene derivatives (compounds **4** and **5**, FigESM.8) [16] and derivative **7** [51], what can be an effect of coordination of these cations by nitrogen atoms of pendant tris-2-pyridylamine moieties.

Results on binding properties in organic solvent can give a general overview of possible interaction in real samples, however, the nature of solvent has enormous impact on host-guest recognition. This is why spectrophotometric response of the tested ligand towards ions in a system containing water was also studied. In acetonitrile:water mixture (9:1, v/v) changes in absorption spectra were observed only in the presence of copper(II) and nickel(II) salts. UV-Vis titration trace for **1** is exemplified with nickel(II) perchlorate experiment (Fig. 2).

Analysis of molar ratio plots indicates that in binary solvent system complexes of 1:1 stoichiometry are formed with stability constants values (log K) 4.60 ± 0.04 and 5.51 ± 0.04 for copper(II) and nickel(II), respectively (Table 1). Not surprisingly, obtained values are lower than binding constant values in pure organic solvent, what may suggest competitive action of water in the host-guest interactions ([52–57], ref. cited therein). It is worth noting that in acetonitrile:water mixture the selectivity of metal cation complexation by **1** increases.

Complexation of copper(II) and nickel(II) cations by amide **1** in mixed solvent system is reversible by addition of equimolar amount of EDTA solution (in the form of disodium salt). Detection limits determined from spectrophotometric titration for copper(II) and nickel(II) ions are: 7.51×10^{-6} mol/dm³ and 2.31×10^{-6} mol/dm³, respectively. The selectivity of copper(II) complexation in the presence

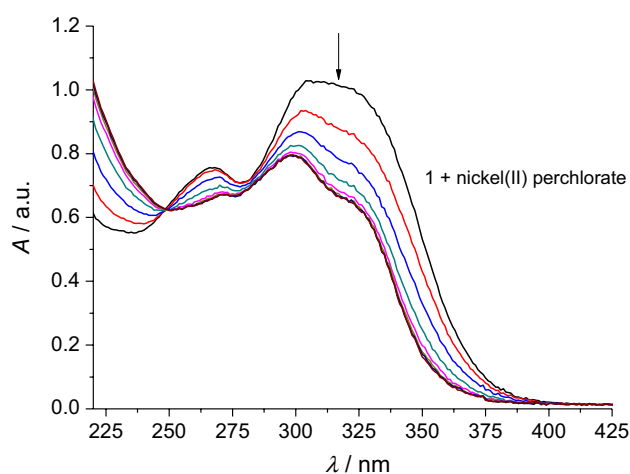


Fig. 2 Changes in UV-Vis spectrum of ligand **1** solution ($c = 2.55 \times 10^{-5}$ mol/dm³) in acetonitrile:water (9:1, v/v) mixture in the presence of nickel(II) perchlorate ($0 \leq R \leq 2.79$). R salt to ligand molar ratio

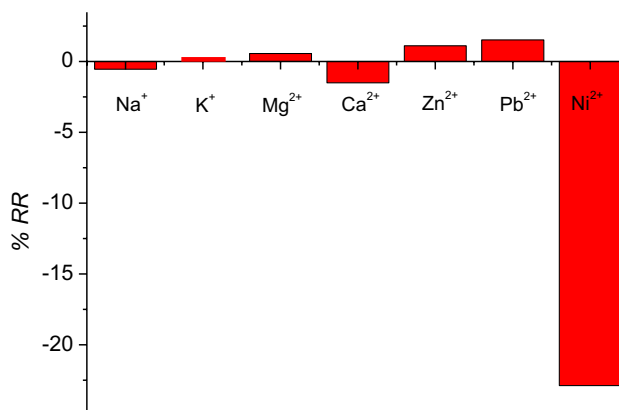


Fig. 3 The influence of metal cation presence (tenfold molar excess) on spectrophotometric response of the ligand solution ($c_1 = 2.38 \times 10^{-5}$ mol/dm³) towards copper(II) perchlorate ($c_{Cu} = 2.31 \times 10^{-5}$ mol/dm³) in acetonitrile:water (9:1) solvent system ($\lambda = 325$ nm)

of interference ions by amide **1** was investigated by studies of the influence of metal cations: Na⁺, K⁺, Mg²⁺, Ca²⁺, Zn²⁺, Pb²⁺, and Ni²⁺ (at tenfold molar excess) presence on spectrophotometric response (as % RR, Fig. 3).

Beside nickel(II) cations, the influence of other ions on spectrophotometric response of ligand towards copper(II) is lower than 5%, that is within the range of the measurement error [58–60]. The presence of nickel(II) ions has an influence on ligand response towards copper(II) cations as both complexes **1**-Cu(II) and **1**-Ni(II) absorb in similar spectral range, and their stability constant values do not differ drastically.

As attempts to obtain metal complexes of **1** in a form of single crystals suitable for X-ray analysis failed, we decided

to suggest the mode of coordination of **1** by spectral methods: ^1H NMR and FT-IR spectroscopy.

^1H NMR spectrometry

^1H NMR spectrum of **1** at ambient temperature in acetonitrile- d_3 shows single set of signals of the proposed in Fig. 4 (top) assignments based on ^1H - ^1H NMR spectrum (FigESM.2) and literature data [61–63]. In the presence of lead(II) perchlorate a signal of amide NH protons (10.3 ppm) is less intense and broadened (Fig. 4, bottom), but not shifted appreciably (0.1 ppm), suggesting eventual non-involvement of the amide proton in coordination [64, 65]. It is also an evidence that metal cation complexation does not cause deprotonation of the **1** as it is often observed for amide ligands. All aromatic proton signals are significantly shifted to higher ppm values suggesting rather strong effect of cation complexation on the aromatic environment of the molecule. Some of these signals have lost their multiplicity and are observed as broaden peaks (what makes difficult to assign signals to the protons). This can be an evidence of fast exchange in acetonitrile in the coordination sphere of the investigated complex or other conformational changes in the system upon metal complexation. For comparison, analogous experiment

was carried out in acetone- d_6 (FigESM.9). Similarly to results observed in acetonitrile- d_3 , ligand spectrum shows single, well-defined set of signals. After addition of lead(II) salt the signals remain sharp contrary to observation in previous solvent. In the complex all signals are shifted downfield. The most significant shift is observed for protons of pyridine pendant groups, particularly C and F, with less pronounced shift of the proton signals of central pyridine skeleton (labeled as A and B). N–H proton signal is slightly downfield shifted (0.2 ppm).

Opposite to lead(II), in a spectrum of zinc complex both in acetonitrile- d_3 and acetone- d_6 at 303 K all proton signals are distorted (Fig. 5 and FigESM.9). In a temperature experiment carried out in acetonitrile- d_3 signals appear more and more flattened and broadened upon heating sample to 341 K. When temperature decreases, signals seem to be more separated and finally, at the lowest possible to achieve in experiment temperature, 228 K the tendency to separation of proton signals is seen, pointing out slower exchange in a frozen state. ^1H NMR experiments show rather intricate equilibrium upon metal cations binding in solution especially in case of zinc(II) (thus signals in the spectrum of the complex cannot be easily ascribed to a particular proton). In cation binding in solution tris-2-pyridylamine pendant residues can be involved with fast exchange of zinc(II) between

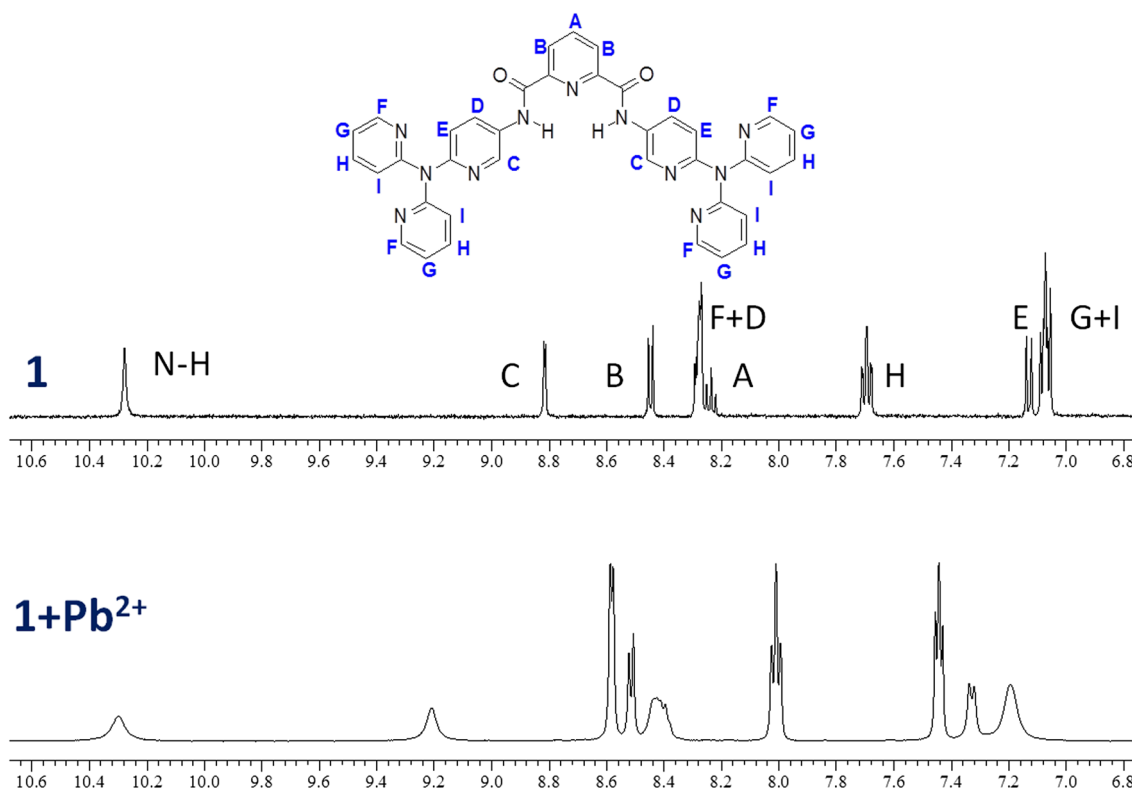
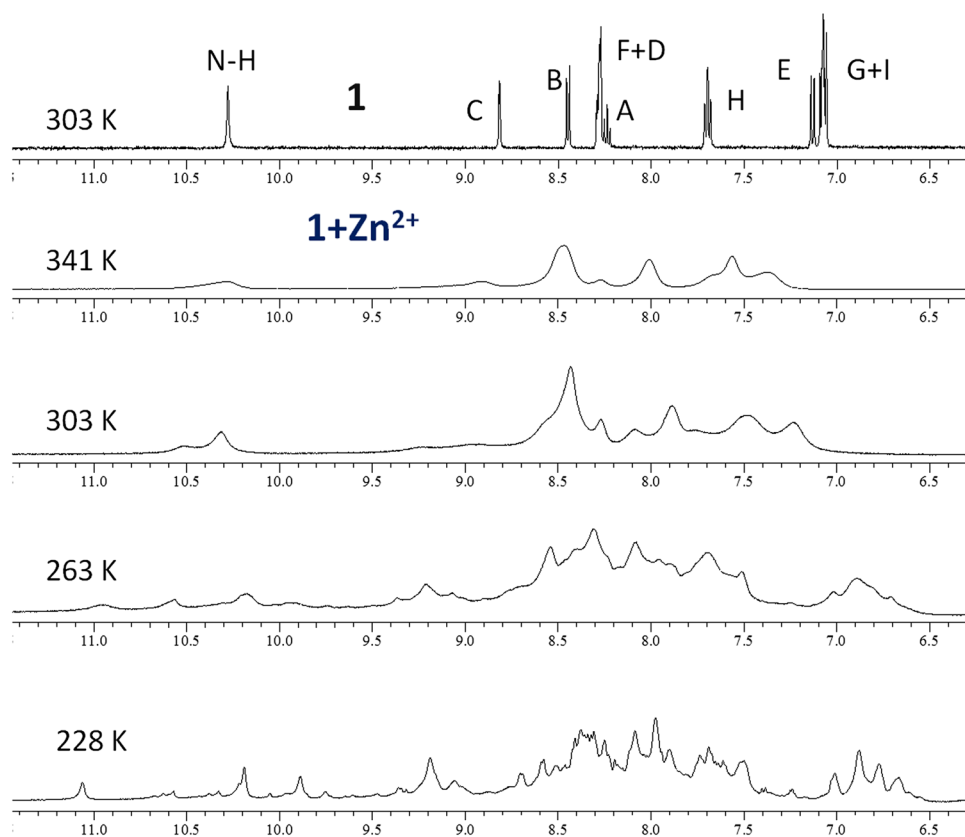


Fig. 4 The comparison of ^1H NMR spectra of the “free” ligand **1** solution (top, with proposed proton assignment) and in the presence of lead(II) perchlorate (bottom) in acetonitrile- d_3 (molar ratio $1:\text{Pb}^{2+} = 1:2$) at ambient temperature

Fig. 5 The comparison of variable-temperature ^1H NMR spectra of ligand **1** (top) and its complex with zinc(II) perchlorate (molar ratio $1:\text{Zn}^{2+} = 1:1$) in acetonitrile- d_3



two bonding centers. On the other hand ligands based on 2,6-pyridinedicarboxamide scaffold and their metal complexes were found to create helices (both in solid state and in solution) of supramolecular architecture dependent on metal cation type [66–71]. The tendency to create helicate system by **1** can be an explanation of the observed behavior of metal complexes in ^1H NMR experiments.

FT-IR spectroscopy

Infrared spectroscopy is widely used as a method for the determination of the mode of metal cation binding by amide ligands [16, 64, 65, 72, 73]. An amide backbone can be engaged in complex formation via oxygen or nitrogen of amide residue what is seen by shift of the I, II, and III amide band. When oxygen atom is involved in complex formation, then I amide band shifts to lower frequencies and II amide band towards higher. A negative shift of II and III amide band is observed when nitrogen atom participates in metal cation coordination. Depending on the type of other functionalities present in amide molecule and their eventual engagement in complex formation the particular region of a spectrum is additionally analyzed. For further studies of the nature of the metal cation complexation by **1**, we studied FT-IR spectra of ligand and its complexes in a solid state,

having in mind that binding mode in solution and in a solid state not necessarily must be the same.

Selected FT-IR spectral bands useful for the investigation of coordination mode of **1** and its metal complexes connected with the vibrations of the amide functionality and pyridine rings with proposed assignments are listed in Table 2. In spectrum of uncoordinated **1** bands characteristic for an amide residue are observed at: 3246 cm^{-1} (νNH)_{trans} characteristic for hydrogen-bonded amide, 1683 cm^{-1} (I amide, $\nu\text{C}=\text{O}$), 1543 and 1533 cm^{-1} (II amide, $\nu\text{C}-\text{N}$, δNH) and 1273 cm^{-1} (III amide, $\nu\text{C}-\text{N}$, δNH). Pyridine ring stretching bands ($\nu\text{C}=\text{C}$, $\nu\text{C}=\text{N}$) are observed at 1590 , 1569 , 1488 , 1471 , 1431 cm^{-1} ; $\delta\text{C}-\text{H}$ in plane vibrations 1389 , 1329 cm^{-1} and out of plane $\gamma\text{C}-\text{H}$ vibrations at 777 and 747 cm^{-1} .

The comparison of partial ($1700\text{--}600\text{ cm}^{-1}$) infrared spectra of uncoordinated ligand and its complexes with lead(II), zinc(II), nickel(II), and copper(II) is shown in Fig. 6. Bands characteristic for perchlorates [74] are observed at ~ 1100 (asymmetric stretching) and ~ 620 (asymmetric bending) cm^{-1} . Band at $\sim 1635\text{ cm}^{-1}$ corresponds to water bending vibration in hydrated perchlorates. Bands corresponding to perchlorate vibrations are listed in Table ESI1.

In all complexes a positive shift of the $\nu\text{N}-\text{H}$ band ($70\text{--}60\text{ cm}^{-1}$), a negative shift of II amide band ($3\text{--}12\text{ cm}^{-1}$) and changes in the spectral pattern of the III amide band suggest the breaking of intramolecular hydrogen bonding

Table 2 Proposed FT-IR band assignments ($\bar{\nu}/\text{cm}^{-1}$) for **1** and its complexes

Assignment	1	1-Pb	1-Zn	1-Ni	1-Cu
$\nu(\text{N-H})$	3246w,br	3317 w	3311 m	3309 m	3444 3335
$\nu(\text{C=O})$ (I amide)	1683 m	1688w (+5)	1676w (-7)	1678w (-5)	no band, shoul- der~1660
$\nu(\text{C=N})$ $\nu(\text{C=C})$	1590 s 1569sh	1594 s 1572sh	1601 s 1570w	(1615w,sh) 1603 m 1582 m	1603 m
$\delta(\text{N-H})$ in plane bending $\nu(\text{C-N})$ stretch (II amide)	1543 m (1533sh)	1531 s	1534 m	1538	1540 m
$\nu(\text{C=N})$ $\nu(\text{C=C})$	1487 m 1471 s 1431 s	1476,1462 d, m 1436 m	1490w 1468 s 1433 s	1467 s 1439 m	1471 s 1435 m
$\delta(\text{C-H})$ ring	1389 m 1329 m	1387 1380 1299	1391 m 1329 m	1392 m 1330 m	1392 m 1320 m
$\nu(\text{C-N})$ stretch $\delta(\text{N-H})$ out-of-plane bending (III amide)	1273 m	1272 1258	1272 m	1287–1254 m, br	1273 m 1252 m
(C-H) out of plane	777w 747w	771 m 756w, sh	771, 752 d(?),br	761w	763 m

Br broad, *s* strong, *m* medium, *w* weak, *sh* shoulder, *d* doublet

(FigESM.10) and confirm that metal cation coordination does not cause deprotonation of the ligand. The comparison of FT-IR spectra of **1** and its lead(II) complex (Fig. 6a) shows the decrease of relative intensity and a slight positive shift of $\nu(\text{C=O})$ band to higher values of wavenumbers ($\Delta\bar{\nu} = +5 \text{ cm}^{-1}$) accompanied by a small shift of bands in the region of II and III amide band towards lower frequencies. These changes—not very spectacular can be rather connected with the change of the chemical environment of the amide group upon complex formation with the engagement of the pendant pyridine residues, than coordination of metal cation with involvement of amide moieties. The last thesis is supported by the slight shift of aromatic ring stretching vibration bands ($\sim 1590 \text{ cm}^{-1}$), towards higher frequencies and the change of bending vibration of pyridine rings signal to one single band 770 cm^{-1} . Characteristic for perchlorate anion band at $\sim 1000 \text{ cm}^{-1}$ in the spectrum of complex is shifted to lower wavenumbers ($\Delta\bar{\nu} = 16 \text{ cm}^{-1}$) in comparison to the spectrum of “free” salt. Signal of perchlorate anion is not split suggesting weak coordination or hydrogen bonding interactions [75, 76].

For both zinc(II) and nickel(II) complexes similar trend of spectral changes (Fig. 6b, c), with some differences in multiplicity and intensity of the particular signals is observed. In both cases I amide band, of less intensity than in uncoordinated ligand, is slightly shifted towards lower frequencies. More significant, than for amide bands, changes are observed for aromatic rings bands, suggesting that the

pendant tris-2-pyridylamine residues are the main coordination center for these metal cations. Perchlorate ion seems not to be engaged in complex formation—as its signal is observed at almost the same position as for free salts. This can be contrary to crystallographic data reported for tris-2-pyridylamine complex with zinc(II) perchlorate, where zinc center is six-coordinated with an octahedral geometry by the two, bidentate ligands (via nitrogen atoms) and two water molecules [43]. The perchlorate ions present in the coordination sphere are linked to coordinated water via hydrogen bonds. Wang et al. [44] described crystallographic structure of tris-2-pyridylamine complex with nickel(II) perchlorate, where metal cation lies on an inversion center and is octahedrally coordinated by nitrogen atoms from all pyridine rings of two ligand molecules. In coordination sphere two perchlorate anions are also present.

Somewhat different spectral pattern in FT-IR spectra was found in case of copper(II) complex of **1** (Fig. 6d). Well observable are changes within signals characteristic for pyridine rings vibrations, what suggests the engagement of these part of the molecule in complex formation. Similar binding mode was described for the structure of the amine complex with copper(II) perchlorate, however, in this case nitrogen atoms of two pyridine rings from two receptor molecules are involved in the metal cation complexation [45]. However, in the investigated here case the most significant change is related to I amide band. In

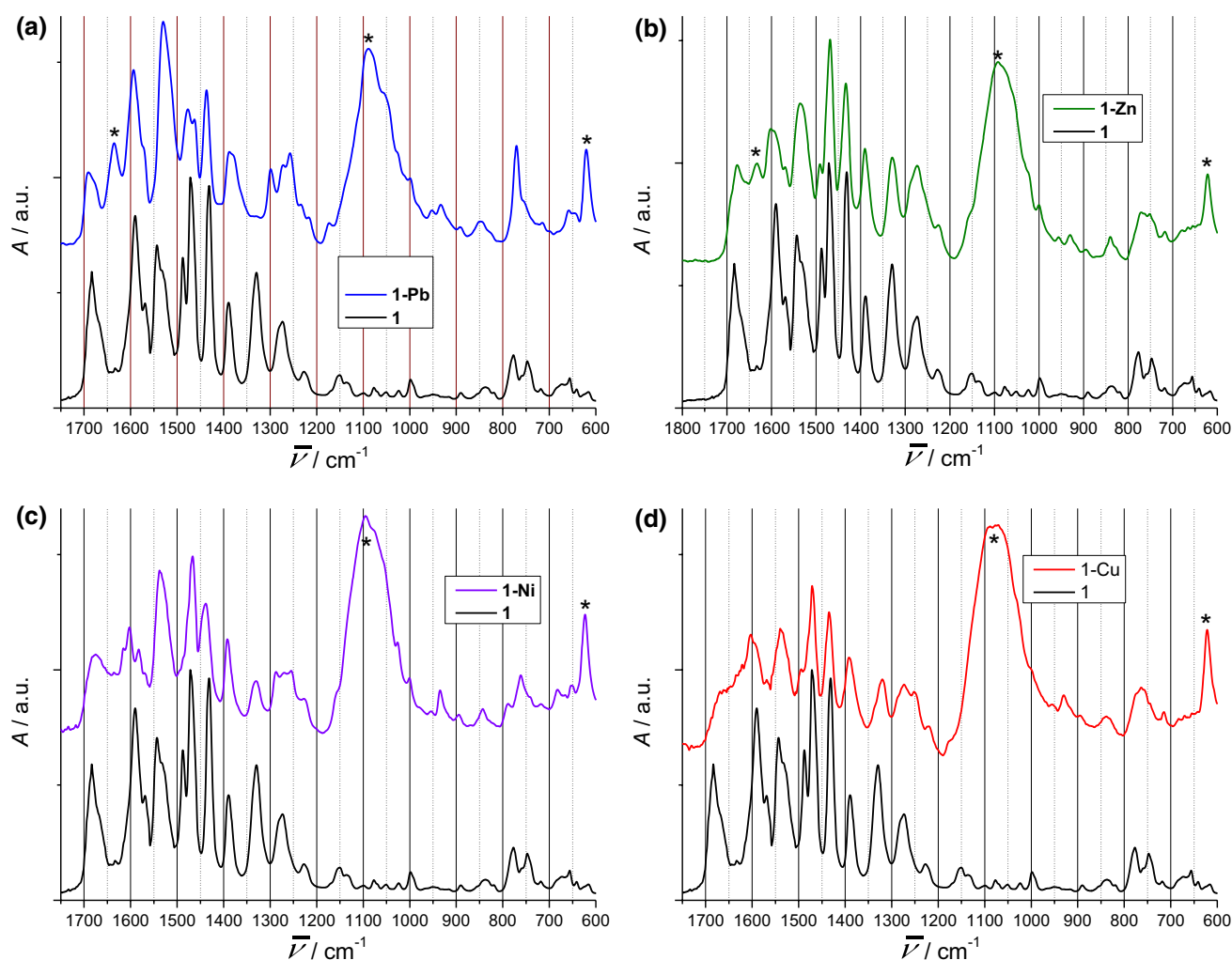


Fig. 6 Partial 1700–600 cm^{-1} FT-IR-ATR spectra (normalized) of **1** and its complex with **a** lead(II), **b** zinc(II), **c** nickel(II), and **d** copper(II) perchlorate. *Signals from perchlorate salts

copper(II) complex, the band characteristic for $\nu(\text{C}=\text{O})$ vibrations almost disappears (or is present as band of extremely low intensity as shoulder at $\sim 1667 \text{ cm}^{-1}$). Similar spectral changes were observed for lanthanide complex of *N,N'*-bis(2-pyridinyl)-2,6-pyridinecarboxamide [77], suggesting enolization and subsequent deprotonation of amide moiety upon metal complexation. The amide-iminol tautomerism was investigated for different types of amides [78–82] in solution and in a solid state. Metal cation triggered tautomerisation was also reported for di-2-picolyamine-based amide which binds zinc(II) cation in imidic acid tautomeric form [83, 84]. On the other hand, II amide band ($1500\text{--}1550 \text{ cm}^{-1}$) is a marker of absence of protons linked to nitrogen atoms of amide groups in a complex [85] so in the case of studied here complex of **1**, enolization and deprotonation of the amide moiety

(cf. Fig. 7) is not so obvious and can be treated only as hypothesis.

Ligand-anion complexation studies

Although our investigations were focused on metal cation complexation, amides as N–H hydrogen bond donors, can also serve as anion receptors. Thus, we studied also the spectrophotometric response of **1** towards anionic species. Among tested anions (halides, nitrates(V), dihydrogenphosphates, carboxylates, hydrogensulfates, hydroxides) spectral changes of the ligand **1** solution in acetonitrile were caused only by the presence of tetra-*n*-butylammonium fluoride and tetra-*n*-butylammonium hydroxide (Fig.ESM.11). Estimation of reliable binding constant value of fluoride complex in UV–Vis titration experiment was not possible due to small spectral changes (FigESM.12). However, fluoride

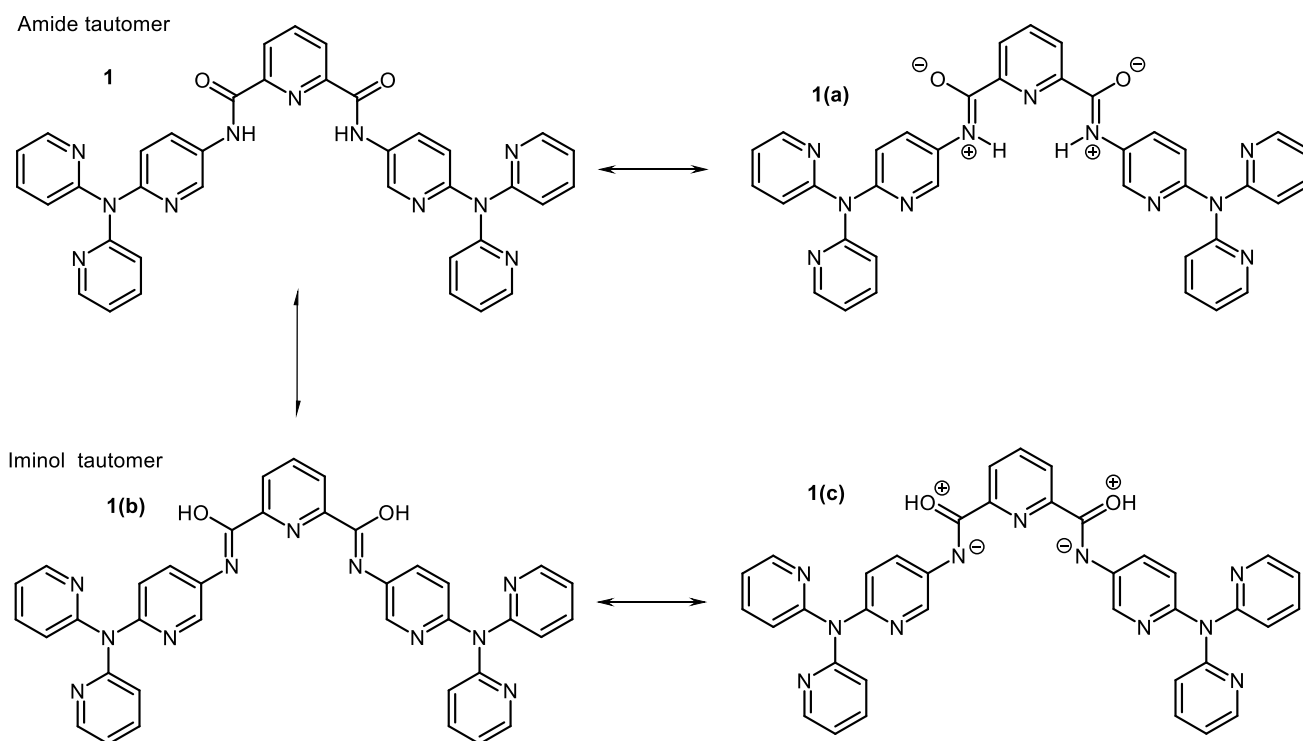


Fig. 7 Possible tautomersim of **1** and its resonance ionic forms of tautomers

anion complexation was confirmed in ^1H NMR experiment, where host and guest are used in higher concentrations. In the ^1H NMR spectrum (acetonitrile- d_3) of ligand **1** registered in the presence of fluoride salt the significant shift of NH proton signal to higher ppm values in comparison with the spectrum of the “free” host ($\Delta\delta = +4.65$ ppm) is observed (FigESM.13), suggesting formation of stronger intermolecular hydrogen bond between anion and amide [20–29, 61–63]. From the NMR titration experiment conducted in acetone- d_6 the stoichiometry and the stability constant value of the complex was estimated using molar ratio and Scott’s method. Molar ratio plot indicates the formation of 1:1 complex, what is confirmed by the Scott’s linear plot (FigESM.14). The stability constant value for fluoride complex was estimated as $\log K \geq 4$ from Scott’s equation [86] being a modified Benesi-Hildebrand [87] equation.

Conclusions

Described here new, tris-2-pyridylamine-based ligand, synthesized with satisfactory yield, interacts with divalent metal cations in acetonitrile and its mixture with water. In acetonitrile:water solvent system (9:1 v/v) selective spectrophotometric response towards copper(II) and nickel(II) perchlorates were found. Detection limits of copper(II) and nickel(II) cations under measurement conditions are

7.51×10^{-6} mol/dm 3 and 2.31×10^{-6} mol/dm 3 , respectively. On the basis of the analysis of ^1H NMR and FT-IR spectra it was assumed, that the main role in metal cation complexation play pendant tris-2-pyridylamine moieties and the central amide residue is not engaged in metal cation complex formation. The most interesting seems to be complex formation with copper(II) cation. Taking into account the importance of copper(II) complexes with amide-type ligands our further efforts are focused for the obtainment of single crystals suitable for X-ray analysis to confirm or exclude statements drawn here. The change of the coordination center in pyridine-2,6-carboxamides, substances of proved biological activity, can be interesting among the others in medical applications of this group of compounds.

Experimental

All chemicals of the highest available purity were purchased from commercial sources and used without further purification (see Table ESM2). The reaction progress and purity of a product was monitored by TLC using aluminium sheets covered with silica gel 60F $_{254}$ (Merck). ^1H NMR and ^{13}C spectra were recorded on Unity 500 Plus apparatus at 500 MHz and at 125 MHz, respectively. ^1H NMR titration experiment was conducted with the use of Bruker Avance III HD spectrometer (400 MHz). Chemical shifts are reported as $\delta/$

ppm values in relation to TMS. FT-IR spectra (ATR, crystal diamond and in KBr pellets) were taken on a Nicolet iS10 apparatus. Mass spectrum was registered on a GCT premier (Waters). UV-Vis titrations were carried out in acetonitrile (LiChrosolv MERCK) and its mixtures with water using an UNICAM UV 300 spectrophotometer. In measurements performed in aqueous solution deionized water (conductivity $< 1 \mu\text{S cm}^{-1}$, Hydrolab, POLAND) was used. Theoretical calculations were performed with Gaussian 09 W rev. D.01 [39] on computers of PL-Grid Infrastructure. Input files were prepared using GaussView [40].

***N,N'*-Bis[6-[di(2-pyridinyl)amino]-3-pyridinyl]-2,6-pyridinecarboxamide (1, C₃₇H₂₇N₁₁O₂)** To the solution of 0.53 g 5-amino-2,2',2''-tris-2-pyridylamine (2 mmol) and 0.28 cm³ triethylamine (2 mmol) in 15 cm³ anhydrous DMF 0.20 g pyridine-2,6-dicarboxylic acid chloride (1 mmol) was added stepwise. The reaction mixture was magnetically stirred at 60 °C for 12 h. Subsequently, to the cooled (r.t.) mixture water was added. The resulting precipitate was filtrated off and the pure product was obtained after crystallization from propan-2-ol. The reaction yield was 70% (0.46 g). White solid; m.p.: 248 °C; TLC: $R_f = 0.81$ (CH₂Cl₂:MeOH 15:2 v/v); ¹H NMR (500 MHz, DMSO-*d*₆): $\delta = 7.05$ (4H, d, $J = 8.3$ Hz), 7.15 (2H, t, $J = 6.8$ Hz), 7.18 (4H, t, $J = 8.8$ Hz), 7.75 (4H, t, $J = 6.3$ Hz), 8.29–8.36 (7H, m), 8.45 (2H, d, $J = 7.8$ Hz), 8.75 (2H, s), 11.2 (2H, s, NH) ppm; ¹H NMR (500 MHz, acetonitrile-*d*₃): $\delta = 7.09$ – 7.05 (8H, m), 7.13 (2H, d, $J = 8.8$ Hz), 7.69 (4H, t, $J = 7.7$ Hz), 8.24 (1H, t, $J = 8.2$ Hz), 8.30–8.26 (6H, m), 8.45 (2H, d, $J = 7.7$ Hz), 8.82 (2H, d, $J = 2.8$ Hz), 10.30 (2H, s, NH) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆): $\delta = 118.8, 120.0, 120.1, 126.2, 132.0, 132.1, 139.08, 140.9, 142.1, 148.6, 149.2, 153.5, 157.2, 162.8$ ppm; FT-IR (KBr pellet): $\bar{\nu} = 3248, 3084, 3008, 1682, 1588, 1528, 1468, 1430, 1328, 1272, 774, 746, 655$ cm⁻¹; UV-Vis (acetonitrile): $\lambda(\epsilon) = 202$ (6.1×10^4), 269 (3.0×10^4), 305 (3.9×10^4) nm; HRMS (EI): m/z calcd. for C₃₇H₂₇N₁₁O₂ (M⁺) 657.2349, found 657.2332.

Ligand-ion interaction studies

Complexation studies were performed by UV-Vis titration of the ligand solution in acetonitrile and its mixture with water with the respective metal perchlorates (for metal cations recognition) or tetra-*n*-butylammonium (TBA) salts (for anion complexation studies). The stock solutions of the ligand ($\sim 10^{-4}$ mol/dm³) and metal perchlorates or TBA salts ($\sim 10^{-2}$ mol/dm³) [16] were prepared by weighing the respective quantities of them and dissolving in pure acetonitrile or its mixture with water (acetonitrile:water = 9:1, v/v) in volumetric flasks. Titrations were carried out in quartz cuvettes with path length of 1 cm with starting volume of the ligand solution 2.3 cm³. The stability constant values were

calculated with the use of OPIUM software on the basis of titration data [47]. The limits of detection (LODs) were calculated from plots $A = f(\text{concentration of metal perchlorate})$ using Eq. (1):

$$\text{LOD} = \frac{3\sigma}{K} \quad (1)$$

where σ is the standard deviation of the blank and K is the slope of the linear calibration range.

In competition studies, the absorbance of ligand solution in the presence of copper(II) perchlorate at fixed concentration (1 equivalent) was recorded before (A_0) and after (A) addition of interfering metal salt in tenfold molar excess. The influence of interfering ions on spectrophotometric response towards copper(II) cations is presented as the relative response $RR\%$:

$$RR\% = [(A - A_0)/A_0] \times 100\%$$

Complex preparation

Samples for ¹H NMR and FT-IR analyses were prepared by dissolving ligand (0.007 mmol) and the respective salt: lead(II) perchlorate (0.014 mmol), zinc(II), copper(II), and nickel(II) perchlorates (0.007 mmol) or tetra-*n*-butylammonium fluoride (0.007 mmol) in 15 cm³ acetone. The resulting mixture was stirred until complete dissolution. After solvent evaporation (reduced pressure), samples were dissolved in acetonitrile-*d*₃ or acetone-*d*₆ to ¹H NMR spectra registration. Similar procedure was applied for complexes preparation for ATR-FT-IR analysis.

Acknowledgements Authors acknowledged support from sources for science GUT Grant No. 033150 and Ministry of Science and Higher Education (Poland), Grant No. 4914/E-359/M/2018. This research was supported in part by PL-Grid Infrastructure. Authors are grateful to the anonymous Reviewer and the handling Editor whose comments helped to improve the manuscript.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Wibaut JP, La Bastide GLC (1933) *Rec Trav Chem* 52:493
- McWhinnie WR, Kulasingam GC, Draper JC (1966) *J Chem Soc A* 1199
- Kulasingam GC, McWhinnie WR (1967) *J Chem Soc A* 1253
- Lancaster JC, McWhinnie WR (1968) *J Chem Soc A* 254
- Lancaster JC, McWhinnie WR (1970) *J Chem Soc C* 2435
- Lancaster JC, McWhinnie WR (1970) *J Chem Soc A* 2673
- Keene FR, Snow MR, Stephenson PJ, Tiekink ERT (1988) *Inorg Chem* 27:2040
- Szczepura LF, Witham LM, Takeuchi KJ (1998) *Coord Chem Rev* 174:5
- Mosny KK, Crabtree RH (1996) *Inorg Chim Acta* 247:93
- Yang W, Schmider H, Wu Q, Zhang YS, Wang S (2000) *Inorg Chem* 39:2397
- Pérez J, Morales D, García-Escudero LA, Martínez-García H, Miguel D, Bernad P (2009) *Dalton Trans* 375
- Karam A, Tenia R, Martínez M, López-Linares F, Albano C, Diaz-Barrios A, Sánchez Y, Catarí E, Casas E, Pekerar S, Albornoz A (2007) *J Mol Catal A: Chem* 265:127
- Kumar P, Gupta R (2016) *Dalton Trans* 45:18769
- Sengar M, Narula AK (2017) *Sens Actuators, B* 241:567
- Alyapyshev M, Babain V, Tkachenko L, Gurzhiy V, Zolotarev A, Ustynuk Y, Glorizov I, Lumpov A, Dar'in D, Paulenova A (2017) *Z Anorg Allg Chem* 643:585
- Łukasik N, Wagner-Wysiecka E, Hubscher-Bruder V, Michel S, Bocheńska M, Kamińska B (2016) *Supramol Chem* 28:673
- Leung W, Ma JX, Yam VWW, Che CM, Poon CK (1991) *J Chem Soc, Dalton Trans* 4:1071
- Abdolmaleki S, Ghadermazi M, Fattahi A, Sheshmani S (2016) *Inorg Chim Acta* 443:284
- Abdolmaleki S, Ghadermazi M (2017) *Inorg Chim Acta* 461:221
- Chmielewski MJ, Jurczak J (2004) *Tetrahedron Lett* 45:6007
- Chmielewski MJ, Jurczak J (2005) *Tetrahedron Lett* 46:3085
- Chmielewski MJ, Jurczak J (2005) *Chem Eur J* 11:6080
- Chmielewski MJ, Jurczak J (2006) *Chem Eur J* 12:7652
- Yamnitz CR, Niegin S, Winter RK, Gokel GW (2010) *Chem Commun* 2838
- Carasel IA, Yamnitz CR, Winter RK, Gokel GW (2010) *J Org Chem* 75:8112
- Wagner-Wysiecka E, Chojnacki J (2012) *Supramol Chem* 24:684
- Dorazco-González A, Flores Alamo M, Godoy-Alcántar C, Höpfl H, Yatsimirsky AK (2014) *RSC Adv* 4:445
- Bazany-Rodríguez IJ, Martínez-Otero D, Barroso-Flores J, Yatsimirsky AK, Dorazco-González A (2015) *Sens Actuators, B* 221:1348
- Ko SK, Kim SK, Share A, Lynch VM, Park J, Namkung W, Busschaert N, Gale PA, Sessler JL, Shin I (2014) *Nat Chem* 6:885
- Sahoo SK, Kim GD, Choi HJ (2016) *J Photochem Photobiol, C* 27:30
- Yan R, Qui S, Tong L, Qian Y (2016) *Chem Speciat Bioavailab* 28:72
- Liu H, Dong Y, Zhang B, Liu F, Tan C, Tan Y, Jiang Y (2016) *Sens Actuators B* 234:616
- Selivanova N, Vasilieva K, Galyametdinov Y (2014) *Luminescence* 29:202
- Zoubi WA, Ko YG (2016) *J Organomet Chem* 822:173
- Sasmal PK, Streu CN, Meggers E (2013) *Chem Commun* 49:1581
- Ito T, Xu Y, Kim SY, Nagaishi R, Kimura T (2016) *Sep Sci Technol* 51:22
- Tiara T, Yanagisawa S, Nagano T, Zhu Y, Kuroiwa T, Koumura N, Kitamoto D, Imura T (2015) *Colloids Surf B* 134:59
- Wagner-Wysiecka E (2012) Łukasik N *Tetrahedron Lett* 53:6029
- Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Petersson GA, Nakatsuji H, Li X, Caricato M, Marenich A, Bloino J, Janesko BG, Gomperts R, Mennucci B, Hratchian HP, Ortiz JV, Izmaylov AF, Sonnenberg JL, Williams-Young D, Ding F, Lipparini F, Egidi F, Goings J, Peng B, Petrone A, Henderson T, Ranasinghe D, Zakrzewski VG, Gao J, Rega N, Zheng G, Liang W, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Throssell K, Montgomery Jr JA, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Keith T, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Millam JM, Klene M, Adamo C, Cammi R, Ochterski JW, Martin RL, Morokuma K, Farkas O, Foresman JB, Fox DJ (2016) *Gaussian 09, Rev. D.01*. Gaussian, Inc, Wallingford, CT
- Dennington R, Keith TA, Millam JM (2016) *GaussView, Version 5.0.9*. Semichem Inc, Shawnee Mission, KS
- Groom CR, Bruno IJ, Lightfoot MP, Ward SC (2016) *Acta Crystallogr Sect B Struct Sci Cryst Eng Mater* 72:171
- Rajput A, Mukherjee R (2013) *Coord Chem Rev* 257:350
- Wang S, Ding X, He W, Huang W (2009) *Acta Crystallogr Sect E Crystallogr Commun* 65:m1424
- Wang S, He W, Huang W (2011) *Acta Crystallogr Sect E Crystallogr Commun* 67:m78
- Boys D, Escobar C, Zamudio W (1992) *Acta Crystallogr Sect C Struct Chem* 48:1118
- Aradhyula BPR, Kaminsky W, Kollipara MR (2017) *J Mol Struct* 1149:162
- Kyvala M, Lukeš I. Program package "OPIUM" available (free of charge) at <http://www.natur.cuni.cz/~kyvala/opium.html>
- Olshin PK, Myasnikova OS, Kashina MV, Gorbunov AO, Bogachev NA, Kompanets VO, Chekalin SV, Pulkin SA, Kochemirovsky VA, Skripkin MY, Mereshchenko AS (2018) *Chem Phys* 503:14
- Rybak-Akimova EV, Nazarenko AY, Chen L, Krieger PW, Herrera AM, Tarasov VV, Robinson PD (2001) *Inorg Chim Acta* 324:1
- May CM (2002) *Centaurus* 10:26
- Bricks JL, Reck G, Rurack K, Schulz B, Spieles M (2003) *Supramol Chem* 15:189
- Steed JW, Turner DR, Wallace KJ (2007) *Core concepts in supramolecular chemistry and nanochemistry*. John Wiley & Sons Ltd, Chichester, p 16
- Wagner-Wysiecka E, Jamrógiewicz M, Fonari MS, Biernat JF (2007) *Tetrahedron* 63:4414
- Wagner-Wysiecka E, Luboch E, Fonari MS (2008) *Pol J Chem* 82:1319
- Konášová R, Dyrtrtová JJ, Kašička V (2016) *J Sep Sci* 39:4429
- Volkova MA, Kuz'mina IA, Usacheva TR, Sharnin VA, Arena G (2018) *Russ J Inorg Chem* 63:687
- Isaeva VA, Sharnin VA (2018) *Russ J Phys Chem A* 92:710
- Aziz AAA (2013) *J Lumin* 143:663
- Shamsipur M, Mohammadi M, Taherpour A, Lippolis V, Montis R (2014) *Sens Actuators, B* 192:378
- Kumawat LK, Mergu N, Singh AK, Gupta VK (2015) *Sens Actuators, B* 212:389
- Chahal MK, Dar TA, Sankar M (2018) *New J Chem* 42:10059
- Bregovic N, Cindro N, Bertosa B, Barisic D, Frkanec L, Uzarevic K, Tomisic V (2017) *Chem Eur J* 23:10396
- Singha NC, Sathyanarayana DN (1997) *J Mol Struct* 403:123
- Zafiroopoulos TF, Plakatouras JC, Perlepes SP (1991) *Polyhedron* 10:2405
- Gudasi KB, Patil SA, Vadavi RS, Shenoy RV, Patil MS (2006) *J Serb Chem Soc* 71:529
- Kawamoto T, Prakash O, Ostrander R, Rheingold AL, Borovik AS (1995) *Inorg Chem* 34:4294

67. Kawamoto T, Hammes BS, Ostrander R, Rheingold AL, Borovik AS (1998) *Inorg Chem* 37:3424
68. Moriuchi T, Nishiyama M, Yoshida K, Ishikawa T, Hirao T (2001) *Org Lett* 3:1459
69. Preston AJ, Fraenkel G, Chow A, Gallucci JC, Parquette JR (2003) *J Org Chem* 68:22
70. Preston AJ, Gallucci JC, Parquette JR (2006) *Org Lett* 8:5259
71. Helttunen K, Annala R, Suhonen A, Itoniemi J, Kalenius E, Aragay G, Ballester P, Tuononen HM, Nissinen M (2019) *Chem Asian J* 14:647
72. Zafiroopoulos TF, Perlepes SP, Ioannou PV, Tsangaris JM, Galinos AG (1981) *Z Naturforsch* 36:87
73. Gudasi KB, Vadavi RS, Shenoy RV, Patil MS, Patil SA (2005) *Transition Met Chem* 30:569
74. Bishop JL, Quinn R, Darby Dyar M (2014) *Am Mineral* 99:1580
75. Tanase S, Gallego PM, Bouwman E, de Gelder R, Reedijk J (2005) *Inorg Chem Commun* 8:680
76. Lewis DL, Dixon Estes E, Hodgson DJ (1975) *J Cryst Mol Struct* 5:67
77. Gudasi KB, Shenoy RV, Vadavi RS, Patil SA (2006) *Spectrochim Acta, Part A* 65:598
78. Fairlie DP, Woon TCh, Wickramasinghe WA, Willis AC (1994) *Inorg Chem* 33:6425
79. Badiger DS, Hunoor RS, Patil BR, Vadavi RS, Mangannavar ChV, Muchchandi IS, Gudasi KB (2012) *J Mol Struct* 1019:159
80. Dunbar RC, Steill JD, Polfer NC, Berden G, Oomens J (2012) *Angew Chem* 124:4669
81. Albright AL, Collins L, Li J, Harris B, White JM (2016) *Aust J Chem* 69:1193
82. Mir JM, Roy S, Vishwakarma PK, Maurya RC (2018) *J Chin Adv Mater Soc* 6:283
83. Xu Z, Baek KH, Kim HN, Cui J, Qian X, Spring DR, Shin I, Yoon J (2010) *J Am Chem Soc* 132:601
84. Xu Z, Yoon J, Spring DR (2010) *Chem Soc Rev* 39:1996
85. Dunbar RC, Polfer NC, Berden G, Oomens J (2012) *Int J Mass Spectrom* 330:71
86. Scott RL (1956) *Recl Trav Chim Pays-Bas* 75:787
87. Benesi HA, Hildebrand JH (1949) *J Am Chem Soc* 71:2703

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.