Syntheses, structural characterization, and thermal behaviour of metal complexes with 3-aminopyridine as co-ligands

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Abstract

Six mixed metal complexes with 3-aminopyridine (3-ampy) as a co-ligand have been synthesized: *catena*-{[M(μ_2 -3-ampy)(H₂O)₄]SO₄·H₂O} (M =Ni (**1**) and Co (**2**)), [Co(3-ampy)₄(NCS)₂] (**3**), [Co(3-ampy)₂(NCS)₂] (**4**), [Co(3-ampy)₄(N₃)₂] (**5**) and *mer*-[Co(3-ampy)₃(N₃)₃] (**6**), (NCS[−]=isothiocyanate ion, N₃[−] azide ion), and characterized by physio-chemical and spectroscopic methods as well as single crystal X-ray and powder diffraction. In the isostructural complexes **1** and **2** single μ_2 -3-ampy links the Ni(II) and Co(II) centers into polymeric chains. The mononuclear Co(II) and Co(III) pseudohalide complexes **3–6** reveal only terminal 3-ampy ligands. The 3-ampy ligands form supramolecular hydrogen bonded systems via their NH₂-groups and non-covalent π - π ring-ring interactions via their pyridine moieties. Thermoanalytical properties were investigated for **1–3**.

Introduction

Aminopyridine ligands have been extensively studied in the synthesis of many coordination metal compounds ranging from simple mononuclear to coordination polymeric compounds (CPs) with different dimensionality. The construction of CPs is attributed to the intriguing structural diversity and the dual functionality of these ligands, which may lead to the formation of 1D or 3D structures [1–19], especially in the presence of other potentially bridging ligands such as pseudohalides [1–3, 13]. Another feature incorporated in this class of compounds is their affinity to show different

hydrogen bonds, N–H $\cdots$ X between the amino NH and a coordinated pseudohalide (X), which tends to extend the structure from 1D to a 3D network. Extra stability can also be generated through π - π stacking interactions between the aromatic pyridyl ligands, which play an important role in stabilizing the resultant polymeric architectures [1–3, 9, 15, 16].

3-Aminopyridine (3-ampy) as one of the aminopyridine series is a simple molecule which can act as monodentate ligand by binding the metal ions in the most common binding mode via the most basic *N*-pyridyl nitrogen (**II**) [2, 7, 15, 19–35] or the least likely binding site of the amino group (**III**) [33, 34]. The latter bonding mode can also be achieved through the *N*-amino donor site of the pyridinium ion (**IV**) [24, 38, 39]. Moreover, the molecule can also, simultaneously bridging two metal ions via the *N*-pyridyl and *N*-amino donor atoms (**I**) [1–17]. Different binding modes of the 3-aminopyridine ligand are summarized in Scheme 1. In some complexes, the 3-ampy was reported to behave as monoprotonated 3-aminopyridinium cation [24, 38, 40–43] or as doubly protonated 3-ammonium pyridinium dication [44, 46]. In an attempt to explore the coordination chemistry (nuclearity, CPs, dimensionality, hydrogen bonding and non-covalent interactions) of 3-ampy with metal ions (Co(II), Ni(II), and Co(III)) in the presence of potentially bridging pseudohalide ligands (N₃[−]=azide anion and NCS[−]=thiocyanate anion), the following study was undertaken.

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Scheme 1 Bonding modes of 3-aminopyridine (3-ampy)

Experimental

Materials and physical measurements

3-aminopyridine was purchased from Aldrich. All other materials were reagent grade quality. Infrared spectra of the solid complexes were performed on a Bruker Alpha P (platinum-ATR-cap). UV-Vis-NIR spectra were recorded with a LS950 Perkin-Elmer Lambda-spectrometer. Thermal analyses were performed on solid samples with using NETSCH STA (N₂ atmosphere; heating rate 10 °C/min). PXRD measurements of the microcrystalline bulk material were performed with a Bruker D8 Advance powder diffractometer. Elemental CHN microanalyses were carried out with an Elementar Vario EN3 analyzer.

Synthesis of the compounds

Synthesis of catena- $\{[\text{Ni}(\mu_2\text{-3-ampy})(\text{H}_2\text{O})_4]\text{SO}_4\cdot\text{H}_2\text{O}\}$ (**1**)

$\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ (0.263 g, 1 mmol), and 3-aminopyridine (0.095 g, 1 mmol) were dissolved in 80 ml H_2O at 90 °C. Upon slow cooling to RT blue crystals of **1** were separated after 2 days (yield: 0.24 g, 71%). Anal. Calcd for $\text{C}_5\text{H}_{16}\text{N}_2\text{NiO}_9\text{S}$ (338.95 g/mol): 17.7% C; 4.8% H; 8.3% N; Found: 17.6% C; 4.8% H; 8.2% N; IR (ATR, cm^{-1}): 3162 (s, br), 1655 (w), 1612 (w), 1593 (w), 1560 (w), 1495 (w), 1455 (w), 1262 (w), 1077 (s), 1043 (s), 1021 (s), 905 (w), 836 (w), 810 (m), 778 (w), 745 (w), 697 (m), 650 (m), 609 (m), 559 (m), 423 (w).

Synthesis of catena- $\{[\text{Co}(\mu_2\text{-3-ampy})(\text{H}_2\text{O})_4]\text{SO}_4\cdot\text{H}_2\text{O}\}$ (**2**)

A procedure similar to that described for **1** was used to synthesize the pink needle-shaped crystals of **2** using $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ (0.28 g, 1 mmol) instead of Ni(II) salt (yield: 0.26 g, 77%). Anal. Calcd for $\text{C}_5\text{H}_{16}\text{CoN}_2\text{O}_9\text{S}$ (339.19 g/mol): 17.7% C; 4.8% H; 8.3% N; Found: 17.5% C; 4.9% H;

8.4% N; IR (ATR, cm^{-1}): 3200 (s, br), 1655 (w), 1611 (w), 1591 (w), 1495 (w), 1454 (w), 1262 (w), 1077 (s), 1010 (s), 905 (w), 810 (w), 724 (w), 680 (m), 649 (m), 613 (s), 554 (m), 524 (m), 418 (w).

Synthesis of $[\text{Co}(\text{3-ampy})_4(\text{NCS})_2]$ (**3**)

A mixture of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.29 g, 1 mmol), KSCN (0.19 g, 2 mmol) and 3-aminopyridine (0.38 g, 4 mmol) were dissolved in 130 ml of distilled H_2O at 75° C for about 15 min. The hot solution was filtered while hot and then slowly cooled to RT. After six days, fine orange-red needle-shaped crystals were obtained (yield: 0.35 g, 64%). Anal. Calcd for $\text{C}_{22}\text{H}_{24}\text{CoN}_{10}\text{S}_2$ (551.56 g/mol): 47.9% C; 4.4% H; 25.4% N; Found: 47.7% C; 4.3% H; 25.6% N; IR (ATR, cm^{-1}): 3405 (w), 3329 (w), 3283 (w), 3191 (w), 3040 (w), 2083 (vs), 1621 (s), 1579 (s), 1485 (m), 1441 (s), 1342 (w), 1292 (m), 1257 (w), 1190 (w), 1128 (m), 1084 (w), 1047 (m), 1023 (w), 961 (w), 939 (w), 895 (w), 846 (w), 816 (m), 795 (m), 737 (w), 696 (m), 640 (s), 547 (m), 516 (w), 479 (w), 415 (w).

Synthesis of $[\text{Co}(\text{3-ampy})_2(\text{NCS})_2]$ (**4**)

KSCN (0.39 g, 4 mmol) and 3-aminopyridine (0.19 g, 2 mmol) were added to a solution containing $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (0.48 g, 2 mmol) dissolved in distilled H_2O (120 ml). The mixture was heated to a temperature of 80–90° C for 2 h and then filtrated while hot. The solution was stored at 40° C for one day where the dark blue crystals which separated were collected by filtration and air-dried (yield: 0.44 g, 60%). Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{CoN}_6\text{S}_2$ (363.33 g/mol): 39.7% C; 3.3% H; 23.1% N; Found: 39.4% C; 3.5% H; 23.1% N; IR (ATR, cm^{-1}): 3446 (w), 3343 (w), 2090 (s), 2071 (vs), 1620 (m), 1578 (m), 1491 (m), 1444 (m), 1351 (m), 1311 (m), 1273 (m), 1189 (m), 1134 (m), 1058 (w), 893 (m), 811 (w), 757 (m), 712 (m), 693 (w), 658 (m), 609 (s), 547 (w), 421 (w).

Synthesis of [Co(3-ampy)₄(N₃)₂] (5) and [Co(3-ampy)₃(N₃)₃] (6)

A mixture of Co(NO₃)₂·6H₂O (0.29 g, 1 mmol), NaN₃ (0.13 g, 2 mmol) and 3-aminopyridine (0.38 g, 4 mmol) were dissolved in distilled H₂O (140 ml) at 95 °C, and the hot solution was filtered and allowed to stand at RT. The pink prism-shaped crystals which separated in the following day were collected by filtration and dried in air (yield: 0.25 g, 48%). Anal. Calcd for C₂₀H₂₄CoN₁₄ (519.46 g/mol): 46.2% C; 4.7% H; 37.8% N; Found: 46.0% C; 4.6% H; 37.9% N; IR (ATR, cm⁻¹): 3445 (w), 3376 (w), 3319 (w), 3216 (w), 2052 (vs), 1628 (w), 1774 (s), 1487 (s), 1439 (s), 1342 (w), 1298 (m), 1261 (w), 1192 (w), 1134 (w), 1091 (w), 1052 (w), 1021 (w), 978 (w), 914 (w), 880 (w), 842 (w), 802 (s), 704 (s), 639 (m), 549 (w), 525 (w), 414 (w).

Slow evaporation of the mother liquor of **5** at RT resulted in the separation of fine green needle-shaped crystals of [Co(3-ampy)₃(N₃)₃] (**6**) after three weeks. During this period, Co(II) was oxidized to Co(III) upon by aerial oxidation (yield: 0.18 g, 39%). Anal. Calcd for C₁₅H₁₈CoN₁₅ (467.37 g/mol): 38.5% C; 3.9% H; 45.0% N; Found: 38.3% C; 3.8% H; 45.2% N; IR (ATR, cm⁻¹): 3422 (w), 3323 (w), 3213 (w), 2004 (vs), 1719 (w), 1603 (w), 1580 (m), 1488 (w), 1447 (w), 1356 (w), 1295 (w), 1264 (w), 1192 (w), 1128 (w), 1086 (w), 1059 (w), 1025 (w), 908 (w), 879 (w), 799 (m), 697 (m), 655 (w), 602 (w), 585 (w), 544 (w), 443 (w).

X-ray crystal structure analysis

The X-ray single-crystal data of the six title compounds were collected on a Bruker-AXS APEX II CCD diffractometer at 100(2) K. The crystallographic data, conditions retained for the intensity data collection and some features of the structure refinements are listed in Table 1. Data collections were performed with Mo-K α radiation ($\lambda = 0.71073$ Å); data processing, Lorentz-polarization and absorption corrections were performed using APEX and the SADABS computer programs [47, 48]. The structures were solved by direct methods and refined by full-matrix least-squares methods on F², using the SHELX [49, 50] program library. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference Fourier maps, assigned with isotropic displacement factors. Geometrical constraints (HFIX) were applied only for H atoms bonded to C atoms. Further programs used: Mercury, PLATON and ToposPro [51–53]. Packing plots are given in the supplementary section (Figs. S1–S6).

Results and discussion

Synthesis, IR and UV-VIS spectroscopy

The synthesis of the complexes **3–5** was straightforward. Reactions of corresponding metal(II) salts with 3-ampy and KSCN (**3** and **4**) or NaN₃ (**5**) in aqueous or aqueous methanol, afforded the corresponding title compounds. Complexes **1** and **2** were obtained by reaction of equimolar amounts of metal(II) sulfate hydrates with 3-ampy from aqueous solutions. The Co(III) azido complex **6** was obtained as by-product in the synthesis of **5** due to air oxidation of the Co(II) in the mother liquor of **5**. The phase purity of the bulk material of solid compounds was checked by XRPD patterns of **1–6** (Figs S7–S12, supplementary section).

In addition to the vibrations of the pyridine moiety of the 3-ampy molecule in the complexes, the IR spectra show the characteristic bands of the pseudohalide ligands. The strong or very strong absorption bands of $\nu_{\text{as}}(\text{SCN})$ and $\nu_{\text{as}}(\text{N}_3)$ in complexes **3–6** are found at 2083 cm⁻¹ (**3**), at 2090 and 2071 cm⁻¹ (**4**), at 2052 cm⁻¹ (**5**) and at 2004 cm⁻¹ (**6**), respectively. The weak to medium strong vibrations of the –NH₂ group occur in the region 3100–3500 cm⁻¹. In case of **1** and **2**, these bands are buried by the broad band at ~3180 cm⁻¹ arising from O–H vibrations of the lattice water molecule and aqua ligands. In **1** and **2**, the ionic nature of the sulfate group is indicated by the appearance of a very strong broad band (ν_3) centered around 1077 cm⁻¹ (**1**), 1077 cm⁻¹ (**2**) and a sharp band (ν_4) at 609 cm⁻¹ for **1** and 613 cm⁻¹ for **2** [2, 28, 29, 54].

The UV–VIS spectrum of solid Ni(II) complex **1** reveals three broad bands centered at 1118 nm, 654 nm and 312 nm corresponding to the electronic transitions $^3\text{T}_{2\text{g}} \leftarrow ^3\text{A}_{2\text{g}}$, $^3\text{T}_{1\text{g}}(\text{F}) \leftarrow ^3\text{A}_{2\text{g}}$, $^3\text{T}_{1\text{g}}(\text{P}) \leftarrow ^3\text{A}_{2\text{g}}$, respectively, for Ni(II) in octahedral geometry [55–58]. The UV–VIS spectra of the solid Co(II) complexes **2**, **3** and **5** exhibit three absorption bands at 1210, 505 and 335 nm for **2**, at 1075, 500 and 372 nm for **3**, and at 1200, 520 and 372 nm for **5**. These bands are assigned to the electronic transitions $^4\text{T}_{2\text{g}}(\text{F}) \leftarrow ^4\text{T}_{2\text{g}}(\text{F})$, $^4\text{T}_{2\text{g}}(\text{P}) \leftarrow ^4\text{T}_{1\text{g}}(\text{F})$, and $^4\text{A}_{2\text{g}} \leftarrow ^4\text{T}_{1\text{g}}(\text{F})$, respectively, for Co(II) in octahedral environment [55–58]. The solid UV–VIS spectrum of Co(II) complex **4** shows absorption bands at 1340 nm, 574 nm and 340 nm, which corresponds to the $^4\text{T}_{2\text{g}} \leftarrow ^4\text{T}_{1\text{g}}$, $^4\text{A}_{2\text{g}} \leftarrow ^4\text{T}_{1\text{g}}(\text{F})$ and $^4\text{T}_{1\text{g}}(\text{P}) \leftarrow ^4\text{T}_{1\text{g}}(\text{F})$, respectively, for Co(II) in tetrahedral environment. The UV–VIS spectrum of solid Co(III) complex **6** shows a broad absorption band centered at ~625 nm corresponding to $^5\text{E} \leftarrow ^5\text{T}_2$ transition in octahedral Co(III) in weak ligand field environment [55–58].

Table 1 Crystallographic data and processing parameters of **1–6**

Compound	1	2	3
Empirical formula	C ₅ H ₁₆ N ₂ NiO ₉ S	C ₅ H ₁₆ CoN ₂ O ₉ S	C ₂₂ H ₂₄ CoN ₁₀ S ₂
Formula mass	383.67	339.19	551.56
System	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	C2/c
<i>a</i> (Å)	7.5852(6)	7.6067(4)	12.5364(13)
<i>b</i> (Å)	8.6483(5)	8.6749(4)	13.5757(14)
<i>c</i> (Å)	10.3214(6)	10.3518(5)	15.7542(16)
α (°)	89.346(3)	89.649(3)	90
β (°)	73.671(3)	73.745(3)	111.848(5)
γ (°)	72.431(2)	72.613(3)	90
<i>V</i> (Å ³)	617.46(7)	623.57(5)	2488.6(5)
<i>Z</i>	2	2	4
θ max (°)	30.381	30.169	33.509
Data collected	46,270	16,402	85,631
Unique refl./ <i>R</i> _{int}	3645 / 0.0631	3666 / 0.0491	4825/0.1144
Parameters/Restraints	202/12	202/12	209/0
Goodness-of-Fit on <i>F</i> ²	1.071	1.063	1.176
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0360/0.0788	0.0313/0.0712	0.0478/0.1106
Residual extrema (e/Å ³)	0.876/−0.706	0.469/−0.551	0.914/−0.770
Compound	4	5	6
Empirical formula	C ₁₂ H ₁₂ CoN ₆ S ₂	C ₂₀ H ₂₄ CoN ₁₄	C ₁₅ H ₁₈ CoN ₁₅
Formula mass	363.33	519.46	467.37
System	Orthorhombic	Monoclinic	Monoclinic
Space group	Pnma	P2 ₁	P2 ₁ /c
<i>a</i> (Å)	9.9591(11)	7.3836(4)	12.2217(8)
<i>b</i> (Å)	12.1512(13)	19.2152(13)	9.4864(7)
<i>c</i> (Å)	12.6272(12)	8.7534(6)	18.1263(13)
β (°)	90	108.439(3)	109.543(2)
<i>V</i> (Å ³)	1528.1(3)	1178.15(13)	1980.5(2)
<i>D</i> _{calc} (Mg/m ³)	1.579	1.464	1.567
θ max (°)	26.326	28.087	27.000
Data collected	11,390	24,378	47,140
Unique refl./ <i>R</i> _{int}	1626 / 0.0379	5480/0.0718	4324/0.0369
Parameters / Restraints	112/2	341/9	300/6
Goodness-of-Fit on <i>F</i> ²	1.384	1.007	1.130
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0599/0.1090	0.0429/0.0773	0.0418/0.1080
Residual extrema (e/Å ³)	0.586/−0.608	0.368/−0.517	0.887/−0.739

Description of the structures

catena-[M(μ₂-3-ampy)(H₂O)₄]SO₄·H₂O} M = Ni (**1**) and Co (**2**)

Perspective views of the isostructural complexes **1** and **2** are given in Figs. 1 and 2, respectively, with main bond parameters are listed in Table S1. The structures consist of [M(3-ampy)(H₂O)₄]²⁺ cations, sulfate anions, and lattice water molecules packing. The complex

cations contain two crystallographically different metal centers. M(1) atom is *trans* coordinated by two hetero N atoms of 3-ampy ligands [M1–N1 = 2.0979(17) for **1** and 2.1446(14) Å for **2**], whereas M(2) is *trans* coordinated by two amino N atoms of two 3-ampy molecules [M2–N2 = 2.1729(18) for **1** and 2.2253(15) Å for **2**], in addition to four aqua molecules for each metal center [M–O from 2.0428(15) to 2.0819(15) Å for **1** and from 2.0546(13) to 2.1100(13) Å for **2**]. The 3-aminopyridine behaves as a N,N'-bidentate bridging ligand generating 1D

Fig. 1 Displacement ellipsoid plot (50% probability) of complex **1**

Fig. 2 Displacement ellipsoid plot (50% probability) of complex **2**

polymeric chains. The metal centers are located at inversion centers. The intrachain $M \cdots M$ distance is 6.7326(4) Å for **1** and 6.6949(5) Å for **2** and the $M2-N2-C4$ angles are 116.96(13)° for **1** and 116.27(11)° for **2**. The inter-chain metal–metal separations are 6.7706(5), 7.5852(6), 7.8462(6) Å for **1** and 6.7734(4), 7.6067(4), 7.8728(4) Å for **2**. There are different types of hydrogen bonds consolidating the crystal structure by generating a supramolecular 3D network (Figs. S1 and S2): (1) $O-H \cdots O$ bonds between oxygen atoms of aqua molecules and lattice water; (2) $O-H \cdots O$ hydrogen bonds between oxygen atoms of the SO_4^{2-} anion and oxygen atoms of aqua molecules and/or lattice water molecules (Table S3). Compounds **1** and **2** are isostructural to Cd(II) [2] and Cu(II) [12] analogous compounds.

[Co(3-ampy)₄(NCS)₂] (3) and [Co(3-ampy)₂(NCS)₂] (4)

Coordination figures with partial atom labeling schemes for **3** and **4** are given in Figs. 3 and 4, the corresponding packing views are shown in Figs. S3 and S4, respectively, and main bond parameters are summarized in Table S2. In the monomeric compound **3**, the Co(II) center has a *trans*-octahedral geometry formed by four terminal 3-ampy ligands and two terminal N-coordinated isothiocyanate anions, whereas the distorted tetrahedron around Co(II) in complex **4** is formed by two 3-ampy ligands and two terminal N-coordinated isothiocyanate anions. The Co–N bond lengths in **3** vary from 2.0831(14) to 2.2119(14) Å, and in **4** from 1.941(4) to 2.016(3) Å. The Co–N–C and N–C–S bond angles vary from 156.89(13) to 170.7(4)° and from 177.28(15) to 179.5(5)°;

Fig. 3 Displacement ellipsoid plot (50% probability) of complex 3

Fig. 4 Displacement ellipsoid plot (50% probability) of complex 4

the N–C bonds vary from 1.155(7) to 1.160(7) and C–S bonds from 1.626(6) to 1.6386(16) Å.

[Co(3-ampy)₄(N₃)₂] (5) and [Co(3-ampy)₃(N₃)₃] (6)

Coordination figures with partial atom labeling schemes for **5** and **6** are given in Figs. 5 and 6, packing views are represented in Figs. S5 and S6, respectively, and main bond parameters are summarized in Table S3. In the monomeric compound **5**, the Co(II) center has a *trans*-octahedral geometry formed by four terminal 3-ampy ligands and two terminal azide anions, whereas the *mer*-octahedral configuration of Co(III) in complex **6** is formed by three 3-ampy ligands and three terminal azide anions. The Co–N bond lengths in **5** vary from 2.107(3) to 2.238(3) Å, and in **6** from 1.945(2) to 1.978(2) Å. The Co–N–N and N–N–N bond angles vary

Fig. 5 Displacement ellipsoid plot (50% probability) of complex 5

Fig. 6 Displacement ellipsoid plot (50% probability) of complex 6

from 122.1(3) to 130.0(3)° and from 175.8(3) to 178.3(4)°; the Nα–Nβ from 1.182(5) to 1.205(3) Å and Nβ–Nγ from 1.155(3) to 1.182(5) Å (with azido Nα atom bonded to metal center). The amino group forms hydrogen bonds of type N–HN to non-coordinated N4 and N8 atoms of the azide anions (Table S4). Non-covalent π···π ring···ring interactions are observed between neighbouring pyridine rings (Table S5).

Analysis of hydrogen bonded networks with ToposPro 5.4.0.2 program reveal **2M4-1** for **1** and **2**, **sql** for **3**, **pcu** for **5** and **hex** topology for **6**, respectively.

Thermoanalytical behaviour of compounds 1–3

The thermogravimetric heating curves for compounds **1** and **2** are shown in Fig. 7. The Ni(II) compound **1** shows the following steps with weight losses:

step 1: $\Delta m = 26.63\%$ (80–245 °C); step 2: $\Delta m = 6.60\%$ (245–405 °C); step 3: $\Delta m = 31.94\%$ (405–550 °C); step 4: $\Delta m = 6.96\%$ (550–975 °C). The Co(II) compound **2** shows the following steps with weight losses:

Fig. 7 Thermal behaviour of complexes **1** (top) and **2** (bottom)

Fig. 8 Thermal behaviour of complex **3**

(195–340 °C); step 3: $\Delta m = 13.43\%$ (340–442 °C); step 4: $\Delta m = 26.45\%$ (442–975 °C). The first step of weight loss is accompanied with a sharp DSC signal at 174.2 °C and 138.8 °C for **1** and **2**, respectively. The weight losses of 26.63% and 26.38% matches quite well with release of one lattice water molecule and four aqua ligands (theoretical: 26.58% and 26.56%) for **1** and **2**, respectively. The anhydrous products show further steps of weight losses by releasing the 3-ampy ligand and the decomposition of the sulfate anion. The residual mass of the Ni(II) sample at 975 °C is 27.87%. Its PXRD pattern indicate a phase mixture with main microcrystalline components identified as Ni_3S_2 and NiO (Fig. S13). The residual mass of the Co(II) sample of 25.16% at 975 °C matches well with Co_9S_8 (theoretical 24.90%) as identified from the PXRD pattern (Fig. S14).

The thermogravimetric heating curve for compound **3** is shown in Fig. 8. $[\text{Co}(\text{3-ampy})_4(\text{NCS})_2]$ shows the following steps with weight losses: step 1: $\Delta m = 34.25\%$ (110–220 °C); step 2: $\Delta m = 34.17\%$ (220–470 °C); step 3: $\Delta m = 15.25\%$ (470–975 °C). The first two steps of weight loss are accompanied with sharp DSC signals at 195.2 °C and 341.3 °C, respectively. The first step of weight loss is accompanied by color change from orange to intensive blue and PXRD pattern of sample separated at 220 °C is identical with that of $[\text{Co}(\text{3-ampy})_2(\text{NCS})_2]$ (**4**), (Fig. S15) confirming the release of two 3-ampy molecules (theoretical 34.13%). The weight loss of second decomposition step indicates further release of remaining two 3-ampy molecules to form intermediate $\text{Co}(\text{NCS})_2$, followed by further decomposition to Co_9S_8 at 975 °C as confirmed by PXRD (Fig. S16). (residual mass: 16.33%, theoretical mass: 15.31%).

Table 2 Selected compounds with 3-ampy bridging ligand

Compound	Dimension	Refcode	Refs.
<i>catena</i> -{[Ni(μ_2 -3-ampy)(H ₂ O) ₄](SO ₄ ·H ₂ O)} (1)	1D		This work
<i>catena</i> -{[Co(μ_2 -3-ampy)(H ₂ O) ₄](SO ₄ ·H ₂ O)} (2)	1D		This work
<i>catena</i> -[Ag(bis(μ -3-ampy))(ClO ₄) ₂]	1D	NEGQOI	[4]
<i>catena</i> -[Cd(μ -5-nitroisophthalato)-(μ -3-ampy)(H ₂ O)]·2H ₂ O	2D	EFEYZ	[5]
<i>catena</i> -[(μ_4 -4-sulfonatobenzoato-O,O',O'',O''')-(μ_2 -3-ampy)-N,N']-bis(triphenylphosphine)-di-silver(i) monohydrate]	3D	HAGGON	[6]
<i>catena</i> -[bis(μ_2 -3-ampy -N,N')-bis(4-cyanobenzoato-O)-copper(ii)]	1D	HEFWUL	[17]
<i>catena</i> -[bis(aqua-(μ_2 -3-ampy -N,N')-(3-ampy)-diisothiocyanato-nickel(ii)) dihydrate]	1D	JAFDEZ	[16]
<i>catena</i> -{[bis(<i>trans</i> -(μ_2 -3-ampy -N,N')-tetra-aqua-cadmium(ii)) disulfate dihydrate]	1D	JAMLAL	[2]
<i>catena</i> -[bis((μ_2 -azido-N,N')-(μ_2 -azido-N,N')-(μ_2 -3-3-ampy -N,N')-cadmium(ii))]]	3D	JAMLEP	[2]
<i>catena</i> -[(μ_2 -adipato-O,O')-bis(μ_2 -3-ampy -N,N')-copper(ii) adipic acid]	2D	KUBYOW	[15]
<i>catena</i> -[(μ_2 -3-ampy)-(μ_2 -1,3-azido)-(μ_2 -chloro)-cadmium(ii)]	3D	LIFWUT	[3]
<i>catena</i> -[(μ_2 -3-ampy -N,N')-(acetato-O,O')-(acetato-O)-(3-ampy-N)-cobalt monohydrate]	2D	NARGAQ	[11]
<i>catena</i> -[(μ_2 -3-ampy -N,N')-(acetato-O)-(acetato-O,O')-(3-ampy)-nickel(ii) monohydrate]	2D	NASHOG	[12]
<i>catena</i> -[bis(μ_2 -3-ampy)-octaqua-di-copper(ii) disulfate dihydrate]	1D	NIKCAM	[12]
<i>catena</i> -[(μ_2 -3-ampy)-bis(μ_2 -thiocyanato)-cadmium]	2D	NOPFAA	[13]
<i>catena</i> -[(μ_2 -3-ampy)-(μ_2 -chlorido)-(chlorido (N,N-dimethylformamide)-nickel(ii)).N,N-dimethylformamide solvate]	2D	QEBZII	[14]
<i>catena</i> -[(μ_3 -nitrate)-tetrakis(μ_2 -3-ampy)-tris(nitrate)-tetrasilver(i)]	3D	QEJOH	[7]
<i>catena</i> -[(μ -aqua)-(μ -3-ampy)-(μ -2-sulfonatoterephthalato)-trisilver]	2D	WAXLEP	[8]
<i>catena</i> -{[bis(μ_2 -N-(4-methylphenyl)sulfonyl)glutamate)-bis(μ_2 -3-ampy)-tris(3-ampy)-di-cadmium hydrate]}	2D	WOLLEQ	[9]

Conclusions

In this work, three coordination polymers are formed through the interaction of metal(II) salts with 3-ampy as a co-ligand namely two 1D systems *catena*-{[Ni(μ_2 -3-ampy)(H₂O)₄](SO₄·H₂O)} (**1**) and *catena*-{[Co(μ_2 -3-ampy)(H₂O)₄](SO₄·H₂O)} (**2**), in addition to the expected monomeric species [Co(3-ampy)₄(NCS)₂] (**3**), [Co(3-ampy)₂(NCS)₂] (**4**), [Co(3-ampy)₄(N₃)₂] (**5**) and *mer*-[Co(3-ampy)₃(N₃)₃] (**6**), where in the latter case Co(II) was oxidized to Co(III). The isolation of the monomeric complexes through the coordination of the most basic pyridine-N-nitrogen is highly predictable. However, the 3-ampy molecule does behave as an “innocent” ligand as it looks. Surprisingly, it is the less basic amino group has very high tendency to coordinate to other metal ion and propagate the formation of polymeric chains with different dimensionality, as this was obvious in complexes **1** and **2**.

In fact, the formation of CPs with 3-ampy reflects the general trend of this molecule to act as a bridging ligand through its two N-atoms. This trend was demonstrated by the isolation of many CPs with different metal ions such as Cd(II), Cu(II), Ni(II), Co(II), Ag(I) and Ag(II) but still the highest majority were obtained with Cd(II) (Table 1). Pseudohalides used here and or those reported in Table 2 behaved as simple terminal monodentate ligands. Other carboxylate (acetate, benzoate, isophthalate, adipate) or oxyanions (nitrate, sulfonylate,...) seem to be more effective as bridging ligands in the presence of 3-ampy in expanding the network chains (Table 2). Another interesting feature is provided by the 3-ampy co-ligand in its complexes is its ability to form supramolecular hydrogen bonded systems via the NH₂-group and non-covalent π - π ring–ring interactions via its pyridine moiety, which adds extra stability to the resulted compounds.

Thermal analysis confirms that [Co(3-ampy)₂(NCS)₂] (**4**) can be obtained at 220 °C by release of two 3-ampy molecules from [Co(3-ampy)₄(NCS)₂] (**3**) starting material. Co₉S₈ is obtained as final decomposition product (975 °C, N₂ atmosphere) in case of Co(II) compounds **2** and **3**.

Supplementary data

CCDC 1982388–1982393 contains the supplementary crystallographic data for **1–6**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@

ccdc.cam.ac.uk. Further supplementary data: bond parameters (Tables S1–S3), hydrogen bond systems (Table S4), non-covalent ring–ring interactions (Table S5); packing plots (Figs. S1–S6), XRD powder pattern (Figs. S7–S12), for compounds **1–6**, respectively; XRD powder pattern (Figs. S13–S16) for decomposition products of **1–3**, respectively.

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Compliance with ethical standards

Conflict of interest The authors declare that there are no conflicts of interest to this work.

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