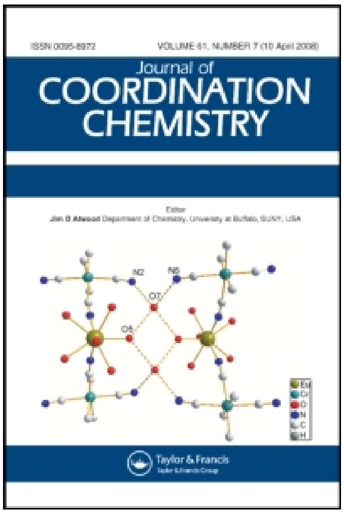

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Cobalt(III), zinc(II), cadmium(II) and palladium(II) complexes with the hydrolysed and non-hydrolysed condensation products of 2-acetylpyridine with ethyl hydrazinoacetate: X-ray structure analysis of *mer*-bis{(*E*)-2-[*N*'-(1-pyridin-2-yl-ethylidene)hydrazino] acetato}cobalt(III) tetrafluoroborate

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Cobalt(III), zinc(II), cadmium(II) and palladium(II) complexes with the hydrolysed and non-hydrolysed condensation products of 2-acetylpyridine with ethyl hydrazinoacetate: X-ray structure analysis of *mer*-bis{(*E*)-2-[*N*′-(1-pyridin-2-yl-ethylidene)hydrazino] acetato}cobalt(III) tetrafluoroborate

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Four Co(III), Zn(II), Pd(II) and Cd(II) complexes with ligands derived *in situ* from acetylpyridine and ethyl hydrazinoacetate or hydrolysed ethyl hydrazinoacetate were prepared. An X-ray structural analysis showed that the Co(III) complex is octahedral with two tridentate (*E*)-2-[*N*′-(1-pyridin-2-yl-ethylidene)hydrazino]acetate (apha) ligands, each forming two five-membered rings with the metal ion. In the tetrahedral Zn(II) complex, only a single apha ligand was coordinated, in the same way as that in the Co(III) complex. In the case of the tetrahedral Cd(II) complex the non-hydrolysed form of (*E*)-2-[*N*′-(1-pyridin-2-yl-ethylidene)hydrazino]acetic acid ethyl ester (aphaoet) coordinated as a bidentate and the two remaining coordination sites were occupied by Cl^- and CH_3COO^- ions. In addition, the square-planar neutral Pd(II) complex was synthesized, having the same bidentate as in the Cd(II) complex and two Cl^- ions in the remaining coordination sites. Due to their being diamagnetic, all four complexes were characterized by ^{1}H-NMR and ^{13}C-NMR spectroscopy.

Keywords: Cobalt(III); Zinc(II); Cd(II); Pd(II); 2-Acetylpyridine; Ethyl hydrazinoacetate; Crystal structure; NMR

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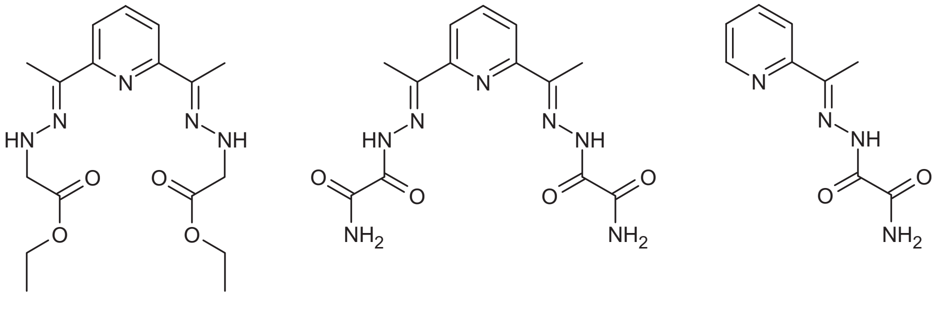
1. Introduction

Studies of donor properties of hydrazones coordinated to transition metals have resulted in the synthesis and structural characterization of quite a number of complexes containing the condensation derivatives of 2,6-diacetylpyiridine [1] and 2-acetylpyridine [2–4]. It has been observed that the Cu(II) and Co(III) complexes bearing the ligand (**1**) (scheme 1), i.e., the condensation product of 2,6-diacetylpyridine (dap) and ethyl hydrazinoacetate (etha), have trigonal bipyramidal geometries. The polydentate in these complexes was found to be coordinated as a tridentate through pyridine and two hydrazone nitrogen atoms, while the remaining two coordination sites were occupied either by monodentate solvent molecules or Cl^- ions [5]. On the contrary, in metal complexes with no CH_2 group between the carbonyl carbon and NH fragment in the side chain, such as the condensation product (**2**) (scheme 1), prepared from 2,6-diacetylpyridine and semioxamazide (sox), pentagonal bipyramidal geometry is favoured. In this case, the polydentate is coordinated *via* pyridine and two hydrazone nitrogen atoms, and two oxygen atoms of carbonyl groups as well, thus forming four five-membered chelate rings at the metal. As a rule, decreased denticity of this ligand was followed by asymmetrical coordination of the side chains and the formation of a six-membered ring. It was demonstrated that the coordination mode depends directly on the electronic configuration of the metal ion and the charge of the ligand, which can be neutral, mono- or dianionic [1].

For complexes of Co(III), Cu(II), Zn(II), Pd(II) and Pt(II) obtained with the condensation derivative of 2-acetylpyridine (ap) and semioxamazide, it was found that the ligand (**3**) (scheme 1) is coordinated as a tridentate through pyridine nitrogen, hydrazone nitrogen and α-oxiazine oxygen, forming two five-membered chelate rings [2–4].

Replacement of semioxamazide in the side chain of **3** by ethyl hydrazinoacetate would prevent coordination of this type, and the synthesis and characterization of the first complexes of transition metals with the condensation product of 2-acetylpyridine and ethyl hydrazinoacetate are described in the present study. In this, we had assumed that the position of the carbonyl oxygen in the side chain of the ligand would enable the formation of a six-membered ring at the metal.



Scheme 1. Structures of the ligands.

2. Experimental

2.1. *Starting materials*

2-Acetylpyridine was obtained from Acros Organics BVBA, Geel, Belgium. Tetrabutylammonium tetrafluoroborate, ethyl hydrazinoacetate hydrochloride, cobalt(II) chloride hexahydrate, zinc acetate dehydrate, cadmium acetate dihydrate and potassium tetrachloropalladate(II) were obtained from Sigma-Aldrich Chemie GmbH, Steinheim, Germany. All solvents were obtained from SINEX Laboratories (Belgrade, Serbia and Montenegro).

2.2. *Preparation of [Co(apha)$_2$]BF$_4$ (4)*

A solution of cobalt(II) chloride hexahydrate (0.12 g, 0.5 mmol), 2-acetylpyridine (0.12 g, 1.0 mmol), ethyl hydrazinoacetate hydrochloride (0.15 g, 1.0 mmol) and tetrabutylammonium tetrafluoroborate (0.16 g, 0.5 mmol) in ethanol (20 cm^3) was refluxed for 30 min. After cooling, several drops of 10% ammonia were added. The dark-red, monocrystalline product [Co(apha)$_2$]BF$_4$ (**4**) separated at room temperature after seven days (yield 61%). Anal. Calcd for $C_{18}H_{20}BCoF_4N_6O_4$ (%): C, 40.8; H, 3.8; N, 15.8. Found: C, 41.0; H, 4.2; N, 15.5. IR (KBr; ν/cm^{-1}): 3304, 3157, 3094, 2960, 1650, 1627, 1604, 1563, 1482, 1376, 1192, 1124, 1078, 1055, 918, 771, 722. ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 2.56$ (s, 3H, N=CCH$_3$), 4.17 (d, 2H, CH$_2$NH, $J =$ 4.8 Hz), 7.71 (distorted t, 1H, NH, $J = 4.8$ Hz), 8.21–8.42 (m, 3H, C-3′H, C-4′H and C-5′H), 9.37 (broad signal, 1H, C-6′H); the number of hydrogen atoms should be doubled as two ligands are bound to Co(III). ^{13}C NMR (50.3 MHz, DMSO-d$_6$): $\delta =$ 12.87 (CH$_3$), 51.44 (NCH$_2$), 124.06 (C-3′), 125.93 (C-5′), 140.15 (C-4′), 150.10 (C-6′), 154.18 (C-2′), 155.50 (C=N), 169.62 (C=O). The molar conductivity ($\lambda_M =$ 130 Ω^{-1} cm^2 mol^{-1}) of an aqueous solution of **4** indicates that it is a 1 : 1 electrolyte.

2.3. *Preparation of [Zn(apha)Cl] (5)*

Into a warm solution of zinc acetate dihydrate (0.22 g, 1.0 mmol) in ethanol (10 cm^3) a warm solution of 2-acetylpyridine (0.12 g, 1.0 mmol) and ethyl hydrazinoacetate hydrochloride (0.15 g, 1.0 mmol) in ethanol (10 cm^3) was added. After refluxing the mixture for 1 h a yellow precipitate of the complex [Zn(apha)Cl] (**5**) separated (yield 63%). Anal. Calcd for $C_9H_{12}ClN_3O_3Zn$ (%): C, 36.9; H, 3.4; N, 14.3. Found: C, 36.9; H, 3.6; N, 14.0. IR (KBr; ν/cm^{-1}): 3426, 3272, 3063, 2920, 1653, 1601, 1480, 1372, 1270, 1209, 921, 791, 675, 639. ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 2.23$ (s, 3H N=CCH$_3$), 3.73 (d, 2H, CH$_2$NH), 7.56 (distorted t, 1H, NH), 7.80–8.14 (4H, aromatic). ^{13}C NMR (50.3 MHz, DMSO-d$_6$): $\delta = 11.22$ (CH$_3$), 52.95 (NCH$_2$), 121.10 (C-3′), 124.58 (C-5′), 137.00 (C-4′), 141.06 (C-6′), 148.74 (C-2′), 149.94 (C=N), 173.06 (C=O). The molar conductivity ($\lambda_M =$ 69 Ω^{-1} cm^2 mol^{-1}) of an aqueous solution of **5** indicates that it is a non-electrolyte.

2.4. *Preparation of [Cd(aphaoet)(AcO)Cl] (6)*

To a warm solution of ethyl hydrazinoacetate hydrochloride (0.18 g, 1.2 mmol) and 2-acetylpyridine (0.14 g, 1.2 mmol) in ethanol (10 cm^3), cadmium acetate dihydrate

(0.31 g, 1.2 mmol) was added. The reaction mixture was heated with stirring at 40°C for 25 min. After cooling to room temperature, a microcrystalline, white precipitate of [Cd(aphaoet)(AcO)Cl] (**6**) was filtered off and washed with ethanol (yield 65%). Anal. Calcd for $C_{13}H_{18}ClN_3O_4Cd$ (%): C, 36.5; H, 4.2; N, 9.8. Found: C, 36.4; H, 4.2; N, 9.8. IR (KBr; ν/cm^{-1}): 3456, 3253, 3107, 3075, 2984, 2910, 1745, 1598, 1550, 1478, 1434, 1374, 1347, 1206, 1178, 1024, 1028, 938, 867, 788, 679. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.19$ (t, 3H, CH_3CH_2, $J = 7.2$ Hz), 1.81 (s, 3H, $OCOCH_3$), 2.21 (s, 3H, $N{=}CCH_3$), 4.09 (q, 2H, CH_2O, $J = 7.2$ Hz), 4.15 (d, 2H, CH_2NH, $J = 4.8$ Hz), 7.13 (distorted t, 1H, NH), 7.36 (ddd, 1H, C-5′H, $^3J_{5',6'} = 5.0$ Hz, $^3J_{5',4'} = 6.8$ Hz, $^4J_{5',3'} = 1.2$ Hz), 7.80–7.88 (m, 2H, C-4′H and C-3′H), 8.58 (dd, 1H, C-6′H, $^3J_{6',5'} = 5.0$ Hz, $^4J_{6',4'} = 1.0$ Hz). ^{13}C NMR (50.3 MHz, DMSO-d_6): $\delta = 11.39$ (CH_3), 14.34 (CH_3CH_2O), 22.00 ($OCOCH_3$), 51.52 (NCH_2), 60.38 (CH_3CH_2O), 120.27 (C-3′), 123.16 (C-5′), 137.88 (C-4′), 141.56 (C-6′), 148.82 (C-2′), 154.36 (C=N), 171.56 (C=O), 177.75 ($OCOCH_3$). The molar conductivity ($\lambda_M = 1.5\ \Omega^{-1}\,cm^2\,mol^{-1}$) of a DMF solution of **6** indicates that it is a non-electrolyte.

2.5. *Preparation of [Pd(aphaoet)Cl$_2$] (7)*

To a suspension of potassium tetrachloropalladate(II) (0.15 g, 0.46 mmol) in water (1.5 cm^3), a solution of ethyl hydrazinoacetate hydrochloride (0.054 g, 0.46 mmol) and 2-acetylpyridine (0.056 g, 0.46 mmol) in ethanol (15 cm^3) was added. The reaction mixture was heated with stirring at 40°C for 40 min and a yellow, microcrystalline product, [Pd(aphaoet)Cl$_2$] (**7**), was obtained. The precipitate was filtered off and washed with water and ethanol (yield 71%). Anal. Calcd for $C_{11}H_{15}Cl_2N_3O_2Pd$ (%): C, 33.2; H, 3.8; N, 10.5. Found: C, 32.9; H, 3.7; N, 10.1. IR (KBr; ν/cm^{-1}): 3224, 3101, 3094, 3073, 3041, 2979, 2907, 1734, 1596, 1481, 1437, 1376, 1337, 1236, 1126, 1109, 1093, 1028, 992, 897, 780, 742, 676. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.23$ (t, 3H, CH_3CH_2, $J = 7.2$ Hz), 2.5 (s, 3H, $N{=}CCH_3$), 3.98 (d, 2H, CH_2NH, $J = 4.8$ Hz), 4.13 (q, 2H, CH_2O, $J = 7.2$ Hz), 7.17 (t, 1H, NH, $J = 4.8$ Hz), 7.79 (ddd, 1H, C-5′H, $^3J_{5',6'} = 5.6$ Hz, $^3J_{5',4'} = 7.6$ Hz, $^4J_{5',3'} = 1.6$ Hz), 8.09 (dd, 1H, C-3′H, $^3J_{3',4'} = 8.0$ Hz, $^4J_{3',5'} = 1.6$ Hz), 8.32 (ddd, 1H, C-4′H, $^3J_{4',5'} = 7.6$ Hz, $^3J_{4',3'} = 8.0$ Hz, $^4J_{4',6'} = 1.2$ Hz), 8.96 (dd, 1H, C-6′H, $^3J_{6',5'} = 5.6$ Hz, $^4J_{6',4'} = 1.2$ Hz). ^{13}C NMR (50.3 MHz, DMSO-d_6): $\delta = 14.21$ (CH_3), 16.08 (CH_3CH_2O), 51.63 (NCH_2), 61.18 (CH_3CH_2O), 126.62 (C-3′), 127.72 (C-5′), 141.52 (C-4′), 149.80 (C-6′), 156.39 (C-2′), 168.52 (C=N), 168.70 (C=O). The molar conductivity ($\lambda_M = 1.0\ \Omega^{-1}\,cm^2\,mol^{-1}$) of a DMF solution of **7** indicates that it is a non-electrolyte.

2.6. *Physical measurements*

IR spectra (KBr; 4000–400 cm^{-1}) were recorded on a Perkin-Elmer FT-IR 1725X spectrophotometer. NMR spectra were obtained using a Varian Gemini 2000 instrument (^{1}H at 200 MHz, ^{13}C at 50.3 MHz). ^{13}C NMR assignments were aided by the use of the DEPT technique to determine numbers of attached hydrogens. Chemical shifts are reported in parts per million (ppm) on the δ scale from TMS as internal standard in the solvents specified. Elemental analyses (carbon, hydrogen and nitrogen) were performed at the microanalysis laboratory at the Faculty of Chemistry, University of Belgrade. Molar conductivities of 1×10^{-3} M solutions in the solvents specified were measured on a Jenway 4010 conductivity meter.

Table 1. Crystal data and structure refinement details for compound **4**.

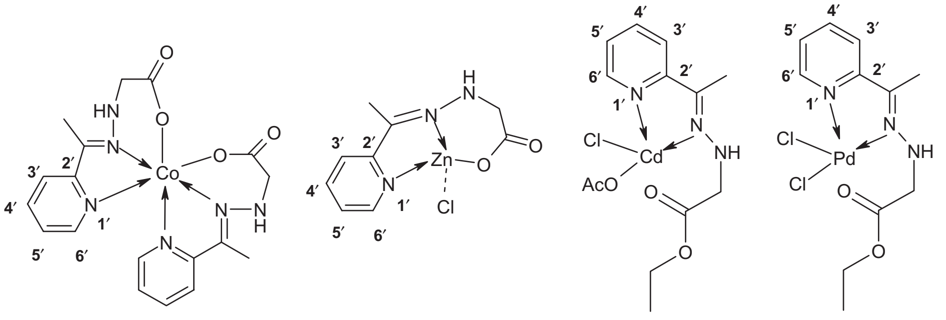
Empirical formula	$C_{18}H_{20}BCoF_4N_6O_4$
Formula weight	530.14
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	$a = 13.513(3)$ Å $b = 18.010(3)$ Å $c = 8.743(2)$ Å
Volume	2127.8(8) Å^3
Z	4
Density (calculated)	1.655 Mg m^{-3}
Absorption coefficient	0.882 mm^{-1}
$F(000)$	1080
θ range for data collection	3–24°
Index ranges	$-15 \leq h \leq 15$, $0 \leq k \leq 20$, $0 \leq l \leq 9$
Reflections collected	3646
Independent reflections	3311 [$R_{int} = 0.0457$]
Completeness to $\theta = 23.97°$	99.4%
Refinement method	Full-matrix least-squares on F^2
Data/Restraints/Parameters	3311/0/317
Goodness-of-fit on F^2	0.786
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0503$, $wR2 = 0.0614$
R indices (all data)	$R1 = 0.1096$, $wR2 = 0.0760$
Absolute structure parameter	−0.06(3)
Largest diff. peak and hole	0.377 and −0.286 e Å^{-3}

2.7. *X-ray diffraction*

A single crystal of **4** suitable for X-ray diffraction was mounted on a glass fibre and X-ray diffraction data were collected on a Philips PW1100 diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å). Relevant details concerning data collection and structure refinement are listed in table 1. Crystals were stable during data collection. Intensity data were processed with a peak-profile analysis procedure and corrected for Lorentz and polarization effects. The structure was solved by direct methods [6] and refined by full-matrix least-squares procedures on F^2 [7], implemented in the WinGX package [8]. Anisotropic displacement parameters were refined for all non-hydrogen atoms, while hydrogen atoms were introduced in calculated positions, with the exception of imine hydrogens, which were located in difference maps and refined isotropically. Final Fourier difference maps were featureless. The absolute structure was assessed using Flack's parameter as implemented in SHELXL97 [7]. Use of PARST [9] and of the Cambridge Crystallographic Database [10] package was made for purposes of the discussion. Complete lists of coordinates, bond lengths, bond angles and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (code 260538).

3. Results and discussion

Four new cobalt(III), zinc(II), cadmium(II) and palladium(II) complexes (**4**–**7**) (scheme 2) containing the ligand obtained by the condensation of 2-acetylpyridine with ethyl hydrazinoacetate, or hydrolysed ethyl hydrazinoacetate, were synthesized.



4 **5** **6** **7**

Scheme 2. Structures of the complexes.

The cobalt(III) complex (**4**) was prepared by reaction of cobalt(II) chloride hexahydrate, 2-acetylpyridine, ethyl hydrazinoacetate hydrochloride and tetrabutylammonium tetrafluoroborate (mol ratio 0.5 : 1 : 1 : 0.5) in ethanol solution. During the reaction, cobalt(II) was oxidized with atmospheric oxygen to cobalt(III). Elemental analysis showed that **4** contains two ligands bound to cobalt(III), these being the hydrolysed condensation product of 2-acetylpyridine with ethyl hydrazinoacetate.

Complex **4** crystallizes in the acentric orthorhombic space group $P2_12_12_1$. The molecular structure of the $[Co(apha)_2]^+$ cation is shown in figure 1, and a list of relevant bond distances and angles is given in table 2. Two monodeprotonated apha$^-$ ligands coordinate to Co^{3+} as tridentates by the pyridine and hydrazine nitrogen atoms and one deprotonated carboxylate oxygen. The ligands are arranged in *mer* geometry, due to the overall preorganized planarity of the apha$^-$ molecules. For each ligand, one five-membered and one six-membered chelate rings are formed; the former are practically planar, while the latter presents a twisted-boat conformation in both cases (puckering parameters following Cremer and Pople [9] are Co–N2–N3–C7–C8–O1, $Q_T = 0.595$ Å, $\varphi_2 = -32°$, $\theta_2 = 103°$; Co–N4–N5–C16–C17–O3, $Q_T = 0.500$ Å, $\varphi_2 = -29°$, $\theta_2 = 113°$). The bischelated complex has Δ absolute configuration and the crystal is optically pure. In the present case spontaneous resolution of Δ and Λ optical isomers occurred during crystallization. The cationic complexes are assembled in helices built by hydrogen bonds between the imine N5–H group of one ligand and the O2 carboxylate of the other on an adjacent molecule (N5–H $\cdots$ O2 ($3/2-x$, $1-x$, $z+1/2$) N $\cdots$ O = 2.940(7) Å, N–H $\cdots$ O = 154(5)°), as indicated in figure 2. All the helices in the crystal are homochiral and they are laterally decorated by BF_4^- anions, hydrogen bonded to the other imine N–H group (N3–H $\cdots$ F2 ($3/2-x$, $1-y$, $z-1/2$) N $\cdots$ F = 2.967(8) Å, N–H $\cdots$ F = 150(5)°).

Starting from $Zn(OAc)_2 \cdot 2H_2O$ or $Cd(OAc)_2 \cdot 2H_2O$, 2-acetylpyridine and ethyl hydrazinoacetate hydrochloride (mol ratio 1 : 1 : 1) in ethanol, the neutral tetrahedral zinc(II) and cadmium(II) complexes, **5** and **6**, were obtained, respectively. In **5**, apha ligand coordinated analogously to the case for the cobalt(III) complex (**4**). The fourth coordination site is occupied by Cl^-. Opposed to this, the cadmium(II) complex (**6**) contains the non-hydrolysed form of the ligand (aphaoet), bound as a bidentate. This complex also contains Cl^- and CH_3COO^- ions as monodentates. $[Pd(aphaoet)Cl_2]$ (**7**) formed by refluxing an ethanolic suspension of $K_2[PdCl_4]$,

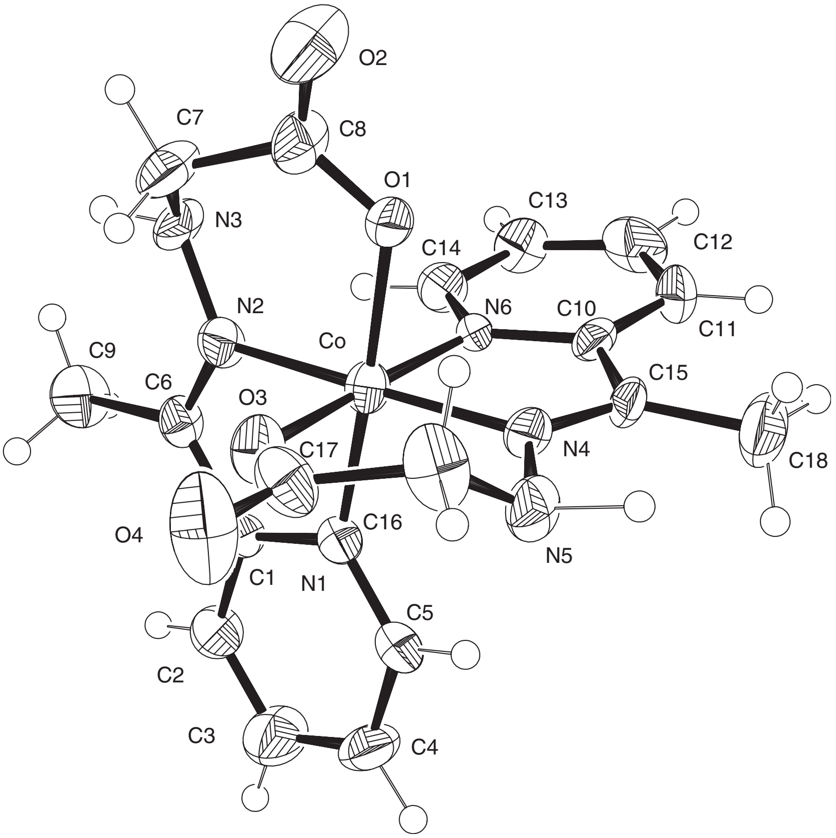


Figure 1. Right-handed helix formed by –N–H $\cdots$ O hydrogen bonds in (**4**). The anions are hydrogen bonded along the helix backbone. Hydrogen atoms are omitted for clarity.

Table 2. Bond lengths (Å) and angles (°) for compound **4**.

Co–O(3)	1.898(5)	N(5)–C(16)	1.482(8)
Co–N(2)	1.913(5)	O(1)–C(8)	1.266(8)
Co–N(1)	1.916(5)	O(2)–C(8)	1.205(8)
Co–O(1)	1.917(5)	O(3)–C(17)	1.233(7)
Co–N(4)	1.922(5)	O(4)–C(17)	1.220(8)
Co–N(6)	1.953(5)	C(1)–C(6)	1.452(8)
N(2)–C(6)	1.289(7)	C(7)–C(8)	1.534(9)
N(2)–N(3)	1.366(7)	C(10)–C(15)	1.472(8)
N(3)–C(7)	1.469(8)	C(16)–C(17)	1.551(9)
N(4)–C(15)	1.301(7)		
N(4)–N(5)	1.381(7)		
O(3)–Co–N(2)	87.4(2)	N(2)–Co–N(4)	176.1(3)
O(3)–Co–N(1)	88.0(2)	O(1)–Co–N(4)	85.7(2)
N(2)–Co–N(1)	81.9(2)	N(1)–Co–N(4)	97.3(2)
O(3)–Co–O(1)	92.5(2)	O(3)–Co–N(6)	178.3(2)
N(2)–Co–O(1)	95.0(2)	N(2)–Co–N(6)	94.0(2)
N(1)–Co–O(1)	176.8(2)	N(1)–Co–N(6)	91.3(2)
O(3)–Co–N(4)	96.5(2)	O(1)–Co–N(6)	88.3(2)
		N(4)–Co–N(6)	82.1(2)

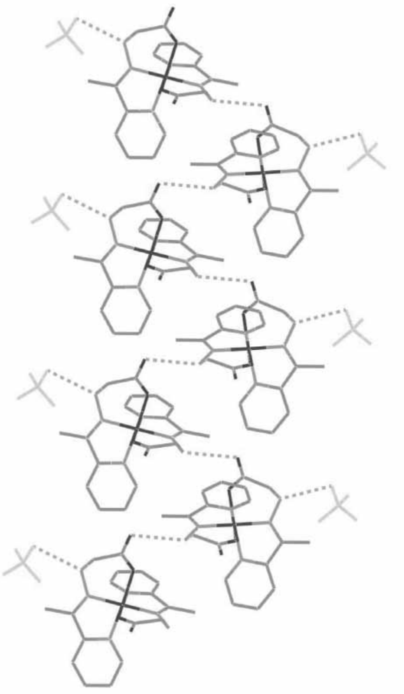


Figure 2. Perspective view and atom labelling scheme for the molecular structure of $[Co(apha)_2]^+$. Thermal ellipsoids are drawn at the 50% probability level.

2-acetylpyridine and ethyl hydrazinoacetate hydrochloride (mol ratio 1 : 1). The polydentate, formed *in situ*, is coordinated in the same way as in the cadmium(II) complex (**6**) to give square-planar geometry at the metal.

Thus, with the apha ligand, the *mer* isomer of the octahedral complex $[Co(apha)_2]BF_4$ (**4**), the tetrahedral complexes [Zn(apha)Cl] (**5**) and [Cd(aphaoet)(AcO)Cl] (**6**) and the square-planar complex $[Pd(aphaoet)Cl_2]$ (**7**) were obtained. Changes in the mol ratio of the metal salt and components of apha during syntheses of the cobalt(III), zinc(II) and cadmium(II) complexes had no effect on the reaction products, but the yields were slightly influenced. It is worth mentioning that, contrary to the Cd(II) and Pd(II) complexes (**6**) and (**7**), the side chain of the coordinated polydentate ligand of the Co(III) and Zn(II) complexes (**4** and **5**) was hydrolysed. This is in agreement with the fact that the radii of Co(III) and Zn(II) are smaller and thus polarization of the ester carbonyl group leading to hydrolysis of the ester is facilitated. This was not the case with Cd(II) and Pd(II), as representatives of the second transition series.

IR spectra of all four complexes exhibit in the solid state $\nu_{N\text{–}H}$ stretching vibrations in the region 3600 to 3200 cm^{-1}. Strong stretching absorptions at 1745 cm^{-1} ($\nu_{C=O}$) and 1206 cm^{-1} ($\nu_{C\text{–}O}$) are present in the IR spectrum of **6**. Analogous bands at 1734 cm^{-1} ($\nu_{C=O}$) and 1206 cm^{-1} ($\nu_{C\text{–}O}$) are assigned to the ester group of **7**. The characteristic band of medium intensity at 1598 cm^{-1} in the case of **6** is due to the C=N group. The same group in the Pd(II) complex absorbs at about 1596 cm^{-1}. The N–N stretch at 1028 cm^{-1} appears also as a medium band in the spectra of both complexes **6** and **7**. A pair of strong asymmetric stretches at 1550 cm^{-1} and an equally strong symmetric stretch at 1434 cm^{-1} are observed only in the spectrum of the Cd(II) complex (**6**), which confirms the presence of the monodentate acetate group. In contrast to these complexes, the Co(III) and Zn(II) complexes (**4** and **5**) give strong bands at 1650 and 1653 cm^{-1}, respectively, caused by the carboxylate group of the organic ligand. In addition, the asymmetric (ν_{COO}) vibration in IR spectra of both complexes is observed slightly above 1600 cm^{-1}. Finally, a rather strong band at 1078 cm^{-1} in the IR spectrum of the Co(III) complex (**4**) is assigned to the BF_4^- ion.

^1H NMR spectra (DMSO-d_6) of the complexes (**4**–**7**) show, in general, a singlet for the $N{=}CCH_3$ group in the range between 2.21 and 2.56 ppm. A common feature of all compounds (**4**–**7**) is the doublet of the methylene group attached to NH, centred at 4.17, 3.73, 4.15 and 3.98 ppm, respectively. The NH proton with a characteristic low-field shift in the region from 7.13 to 7.71 ppm appears as a triplet with $J = 4.8$ Hz and, as expected, this proton can be quickly exchanged by adding D_2O. Regarding the aromatic protons in the pyridine moiety of the complexes, it should be added that the vicinal coupling constants, $^3J_{HH}$, of pyridine correlate nicely with the positions of the coupling protons. For instance, for the Pd(II) complex (**7**), it is observed that a clear difference between the protons in the C-5′ and C-6′ positions ($^3J_{5',6'} = 5.6$ Hz), and C-5′ and C-4′ positions as well ($^3J_{5',4'} = 7.6$ Hz), was seen. It should be noted that the proton at C-5′ which resonates at 7.79 ppm, splits into a threefold doublet with a third coupling constants of 1.6 Hz (*meta* coupling $^4J_{5',3'}$). The same $^3J_{HH}$ coupling pattern was applied to make distinction between protons at C-4′ and C-5′ positions, and those at C-4′ and C-3′.

In the ^1H NMR spectrum of the Cd(II) complex (**6**), where no hydrolysis of the ester group occurs, the triplet at 1.19 and the quartet at 4.09 ppm of the ethoxy group appear, with the common coupling constant of 7.2 Hz. Similar signals are present in the spectrum of the Pd(II) complex (**7**). Furthermore, in the case **6**, the methyl signal of the acetate group attached to cadmium atom resonates at 1.81 ppm, whereas the corresponding signals of the ethoxy group and methyl group in the ^{13}C NMR spectrum appear at 60.38 (CH_2), 14.34 and 22 ppm (Me from OAc). As indicated, the third singlet at high field (11.39) is assigned, by the DEPT technique, to the C-1 imine atom. At low field, two resonances at 171.56 and 177.75 ppm support the presence of two carbonyl groups. ^{13}C NMR spectra of **4**, **5** and **7** show that each contains only one singlet in this region (at 169.62 for **4**; 173.06 for **5**; 168.70 for **7**). At the level needed for structural verification, this undoubtedly supports the presence of one carbonyl group.

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