

COORDINATION
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Synthesis, Molecular, and Crystal Structure of a Complex of Pentacoordinated Zinc with Chloride Ions and Pyridine-2-Carbaldehyde Hemiacetal

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Abstract—The reaction between pyridine-2-carbaldehyde and zinc chloride in wet MeCN yielded a zinc chelate complex with hemiacetal formed in situ from the hydrated pyridine-2-carbaldehyde and the second molecule of pyridine-2-carbaldehyde. According to X-ray diffraction data, the pentacoordinated environment of the zinc ion is formed by two chlorine atoms and the N,N',O-tridentate ligand. In the crystal, molecules are combined into a 3D supramolecular framework due to the intermolecular hydrogen bonds O—H...Cl, C—H...Cl, and π – π stacking interactions between pyridine rings.

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Pyridine and its derivatives are key structural fragments of biologically active natural substances (vitamin B6 and vitamin PP) and some pharmaceuticals (mexidol, cardiamin, emoxypine, and pyritinol) [1]. Of this series, pyridine-2-carbaldehyde and its metal complexes with rare earth elements [2, 3], noble metals [4, 5], and transition metals [2, 6–11] are of particular interest. The presence of two donor centers (N and O) in pyridine-2-carbaldehyde makes it possible to obtain metal complexes with the participation of only the nitrogen atom [4, 5] or chelate structures [2, 3, 5–11], which are prospective precursors to prepare, for example, drugs against Alzheimer's disease, Wilson disease, thalassemia, etc. [12].

The literature data on the coordination of zinc ions with pyridine-2-carbaldehyde are limited [8, 13, 14]. It is known that such reactions in dry MeCN proceed to form chelate complex (pyridine-2-carbaldehyde)₂ · ZnHal₂ [8, 13, 14], while the addition of water to the reaction mixture (the molar ratio of carbaldehyde : ZnCl₂ : H₂O = 2 : 2 : 1, ether) leads to the formation of complex [(pyridine-2-carbaldehyde)₂(H₂O) · Zn—Cl—ZnCl₃] [14].

In order to synthesize new metal-complex compounds based on pyridine-2-carbaldehyde (I), we studied the interaction of the latter with zinc chloride in acetonitrile in the presence of water. Here, we report the synthesis and crystal structure of the zinc complex prepared based on the hemiacetal derivative of pyridine-2-carbaldehyde generated in situ in wet acetonitrile. The formation of this ligand was first observed in the reaction between pyridine-2-carbal-

dehyde and a mixture of Dy(NO₃)₃ · 6H₂O (or Gd(NO₃)₃ · 6H₂O) and Cu(OAc)₂ · H₂O in the presence of triethylamine (MeCN/MeOH as a solvent). However, in the complexes prepared, the metal ion (Dy or Gd) is coordinated only by the oxygen atoms of hydroxyl groups, one of which being deprotonated. The yield of complexes did not exceed 5% [15].

EXPERIMENTAL

Synthesis of {bis[hydroxy(2-pyridinyl)methyl ester]dichlorozinc(II)}. A solution of pyridine-2-carbaldehyde (I) (1.00 g, 9.33 mmol) in wet MeCN (dry MeCN (6 mL) + H₂O (0.10 g, 5.6 mmol)) was added to a solution of ZnCl₂ (0.635 g, 4.66 mmol) in the same solvent (dry MeCN (6 mL) + H₂O (0.10 g, 5.6 mmol)) with stirring. The resulting mixture was stirred at room temperature for 2 h, followed by the addition of diethyl ether (12 mL). The precipitated light yellow powder was filtered off, washed with diethyl ether, and dried in vacuum. Yield, 1.36 g (79%). Yellowish crystals were obtained from MeCN by slow evaporation of the solvent (after a week), mp = 150–151°C.

IR spectrum (ν , cm⁻¹): 3300, 3086, 3036, 2921, 1610, 1488, 1451, 1422, 1409, 1344, 1301, 1264, 1247, 1159, 1142, 1107, 1052, 1007, 890, 879, 849, 779, 757, 709, 668, 646, 627, 540.

For C₁₂H₁₂Cl₂N₂O₃Zn anal. calc. (%): C, 39.11; H, 3.28; Cl, 19.24; N, 7.60.

Found (%): C, 39.18; H, 3.22; Cl, 19.59; N, 7.50.

Table 1. Crystallographic data, details of data collection, and characteristics of data refinement of the structure of **II**

Molecular formula	ZnCl ₂ C ₁₂ H ₁₂ N ₂ O ₃
FW	368.53
<i>T</i> , K	100(2)
Crystal system	Monoclinic
Crystal size, mm	0.13 × 0.20 × 0.21
Space group	<i>P</i> 2/ <i>n</i>
<i>a</i> , Å	8.2157(7)
<i>b</i> , Å	7.3980(7)
<i>c</i> , Å	11.3818(10)
α , deg	90.030(3)
β , deg	90.024(3)
γ , deg	89.994(3)
<i>V</i> , Å ³	691.78(11)
<i>Z</i>	2
ρ_{calc} , g/cm ³	1.759
μ , mm ⁻¹	2.167
θ range, deg	2.48–27.00
Number of collections: collected	8269
unique (<i>N</i>)	2874 [<i>R</i> _{int} = 0.0425]
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.1010, 0.2422
<i>R</i> ₁ , <i>wR</i> ₂ (for <i>N</i>)	0.1088, 0.2459
GOOF	1.345

Table 2. Selected bond lengths and bond angles in compound **II**

Bond	<i>d</i> , Å	Angle	ω , deg
Zn(1)–Cl(1)	2.27(1)	O(1)Zn(1)N(1)	72.7(3)
Zn(1)–O(1)	2.20(1)	Cl(1)Zn(1)Cl(1)	111.7(1)
Zn(1)–N(1)	2.07(1)	Cl(1)Zn(1)N(1)	98.5(3)
O(1)–C(6)	1.43(1)	N(1)Zn(1)N(1)	145.5(4)
O(2)–C(6)	1.31(2)	O(1)Zn(1)Cl(1)	124.2(3)

Table 3. Geometric parameters of hydrogen bonds in the structure of **II**

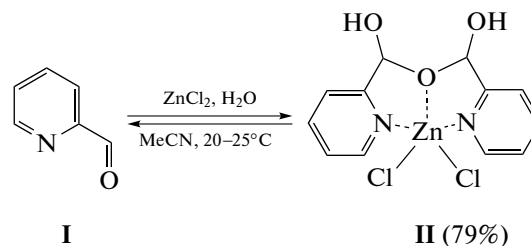
Bond D–H...A	Distance, Å			Angle D–H...A, deg
	D–H	H...A	D...A	
O(2)–H(2)...Cl(1)	0.82	2.27	3.07	164.6
C(2)–H(2)...Cl(1)	0.93	2.91	3.70	143.9

X-ray diffraction study was performed on a BRUKER D8 VENTURE PHOTON 100 CMOS diffractometer (MoK α radiation, $\lambda = 0.71073$ Å). The structure of the compound was determined and

refined by direct methods using the SHELXL software [16]. Absorption corrections were applied with the SADABS multi-scan method. The non-hydrogen atoms were refined in the anisotropic approximation using the SHELX software. The coordinates of the hydrogen atoms were calculated geometrically. The crystallographic data and the structure refinement parameters are given in Table 1; selected bond lengths are listed in Table 2. The structural data for compound **II** were deposited with the Cambridge Structure Database (CCDC no. 1531385).

RESULTS AND DISCUSSION

When zinc chloride was allowed to react with two equivalents of pyridine-2-carbaldehyde (**I**) and water (with the molar ratio equal to 1 : 2 : 2) at room temperature (2 h, MeCN), rare five-coordinated zinc complex **II** was prepared with a yield of 79% (Scheme 1).

**Scheme 1.**

Complex **II** is a light yellow powder soluble in H₂O, EtOH, DMSO, acetone, and MeCN and insoluble in diethyl ether, CHCl₃, and THF. Crystals of complex **II** were obtained from MeCN by slow evaporation of the solvent.

According to X-ray diffraction data, the asymmetric unit contains two molecules of the complex (two enantiomers, RR and SS). The Zn(II) atom lying on the twofold axis is coordinated by two chlorine atoms and the chelating N,N',O-tridentate ligand bound to the metal ion through two nitrogen atoms of two pyridine rings and an oxygen atom of hemiacetal (Fig. 1). Based on the value of the structural distortion index τ_5 ($\tau_5 = 0.36$) [17], the coordination polyhedron of the Zn(II) atom can be described as a distorted square pyramid. The five-member chelate cycle Zn–O–C–C–N has an envelope conformation and is almost coplanar with the pyridine ring (the deviation from the plane for the C₆ atom is 0.232 Å). The torsion angle C(5)N(1)Zn(1)O(1) is -1.3° . The ZnCl₂ plane is almost perpendicular to the coordination core ZnNON (dihedral angle is 88.33°). The OH groups are directed in the opposite directions relative to the ligand plane. The Zn–N bond (Fig. 1) is shorter (by ~ 0.03 Å) than analogous bonds in the structurally similar complex [2,2'-(oxidimethylene)dipyridine]dichlorozinc (**II**) [18].

The crystal structure of complex **II** is shown in Fig. 2. The shortest intermolecular contact is the contact between the chlorine and hydrogen atoms of the OH

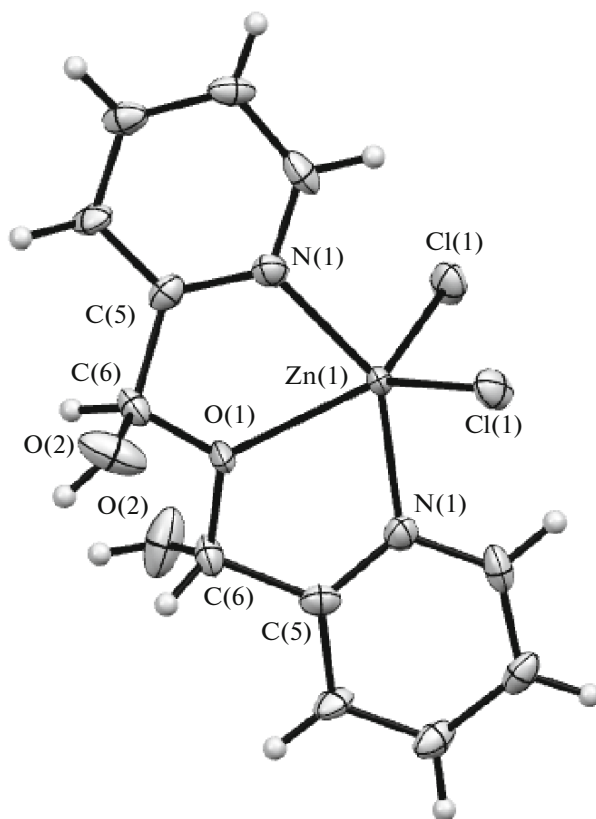
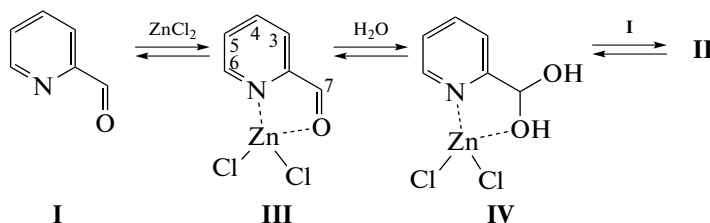


Fig. 1. Molecular structure of complex II.

groups of neighboring molecules (2.27 Å) oriented to each other in the “head-to-tail” manner. The indicated hydrogen bonds of the O–H⋯Cl type (the sum of the van der Waals radii of the H and Cl atoms is 3.01 Å [19]) lead to the formation of chains (Fig. 2, Table 3). The chains are almost parallel to each other (the angles between their planes do not exceed 0.19°) and are combined into a 3D supramolecular structure by means of short contacts that can be classified as weak hydrogen bonds of the C–H⋯Cl type (2.91 Å) [19] (Fig. 3, Table 3) and π – π -stacking interactions (3.68 Å) between pyridine rings (Fig. 4).

The possible mechanism of the reaction (Scheme 2) involves the formation of intermediate chelate complex III from pyridine-2-carbaldehyde (I) and zinc chloride, which in the course of hydration is converted into complex IV. When hydrate IV was allowed to react with starting pyridine-2-carbaldehyde or its zinc chelate III, complex II is formed. It was shown [20] that zinc or cobalt ions increase the hydration efficiency of pyridine-2-carbaldehyde by a factor of $\sim 10^7$, but the possibility of the following formation of the acetal was beyond the scope of this work.



Scheme 2.

In the IR spectrum of complex II there is no absorption of the carbonyl group at 1713 cm^{-1} , but an intense band is observed at 3300 cm^{-1} , which is

explained by the presence of the hydroxyl group. The appearance of a strong broadened band at 1007 cm^{-1} indicates the presence of C–O (C–OH and C–O–C)

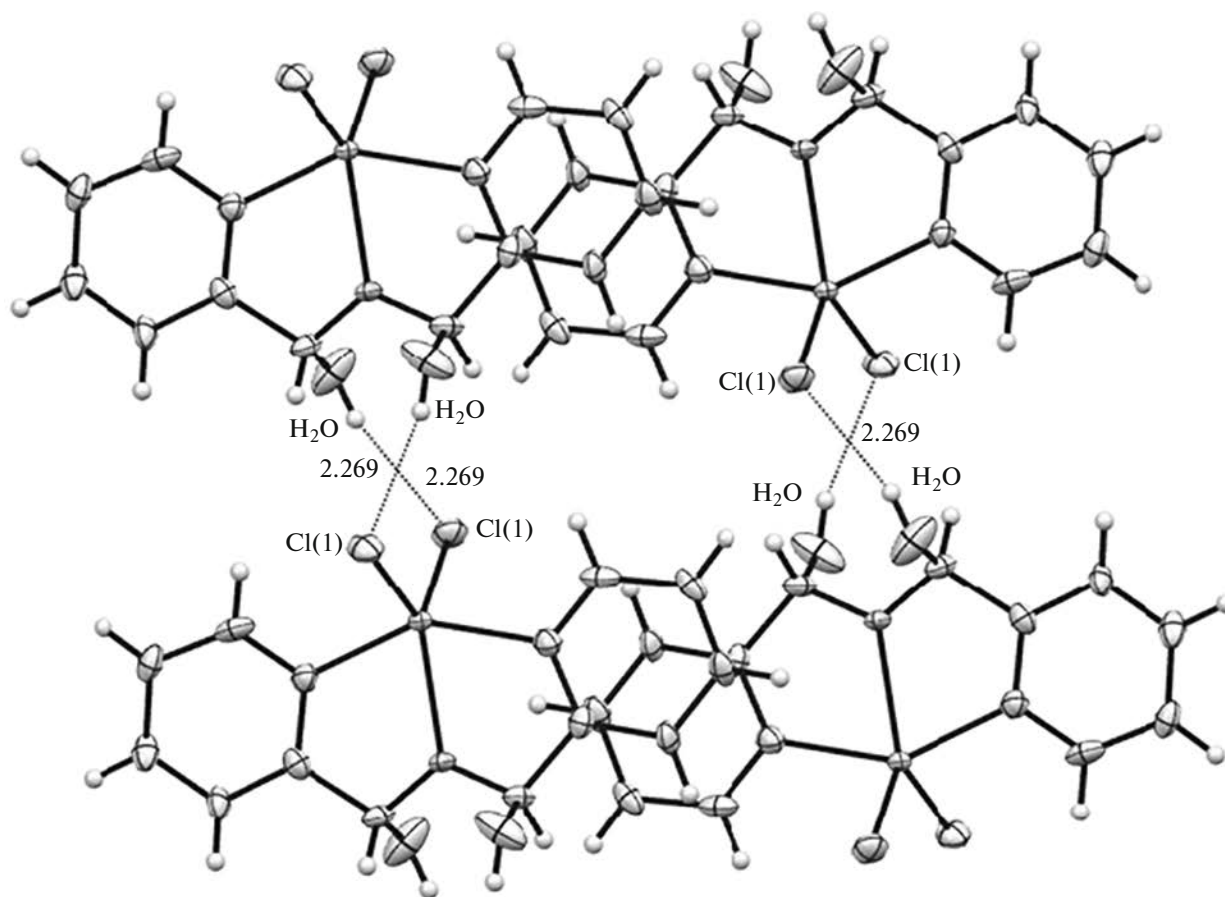


Fig. 2. Fragment of the crystal structure of **II** with hydrogen bonds O–H···Cl between neighboring molecules.

bonds. The band of C=N stretching vibrations of the pyridine ring in complex **II** at 1610 cm^{-1} is shifted to the short-wavelength region (by 25 cm^{-1}) as compared to the analogous band (1585 cm^{-1}) of starting pyridine-2-carbaldehyde, which testifies in favor of the coordination of the zinc ion by the pyridine nitrogen atom.

According to the NMR data, complex **II** does not retain its structure in solution. In the ^1H and ^{13}C NMR

spectra (DMSO- d_6 and MeCN- d_3) of complex **II**, signals of the pyridine ring and aldehyde group (~ 10 ppm (H) and ~ 194 ppm (C)) are observed, which are characteristic of pyridine-2-carbaldehyde. In the ^1H and ^{13}C NMR spectra of an aqueous solution (D_2O) of the complex, signals of the hem-diol form of the pyridine ligand (6.15 and 89.7 ppm) in an amount 10 times greater than that of the aldehyde ligand are observed. Obviously, in water, the equilibrium of hemiacetal \leftrightarrow

Table 4. Chemical shifts (δ , ppm) of protons in the spectra of free and coordinated pyridine-2-carbaldehyde and its hem-diol (atom numbering is shown in Scheme 2)

Compound (solvent)	H ³	H ⁴	H ⁵	H ⁶	H ⁷
Pyridine-2-carbaldehyde (DMSO- d_6)	7.82	7.91	7.57	8.72	9.93
Complex II (DMSO- d_6)	7.93 (+0.11)	8.06 (+0.15)	7.72 (+0.15)	8.83 (+0.11)	9.99 (+0.06)
Pyridine-2-carbaldehyde (MeCN- d_3)	7.91	7.94	7.59	8.77	10.00
Complex II (MeCN- d_3)	8.06 (+0.15)	8.09 (+0.15)	7.74 (+0.15)	8.91 (+0.14)	10.07 (+0.07)
Hem-diol (D_2O)	7.52	7.93	7.32	8.38	5.91
Complex II (D_2O)	7.71 (+0.19)	8.05 (+0.12)	7.56 (+0.24)	8.46 (+0.08)	6.15 (+0.24)

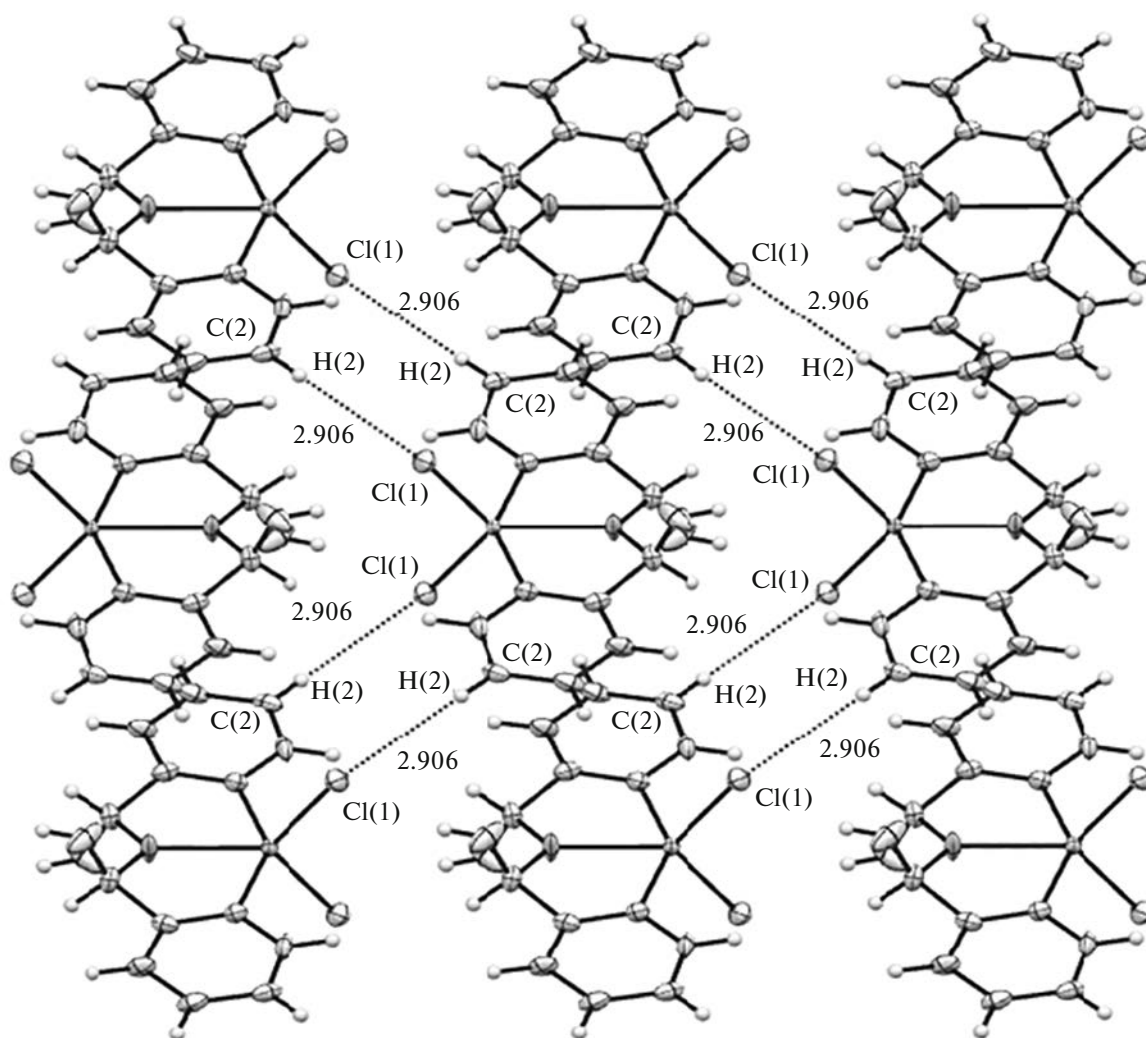


Fig. 3. Fragment of the crystal structure II with hydrogen bonds C–H...Cl between the molecules of neighboring chains.

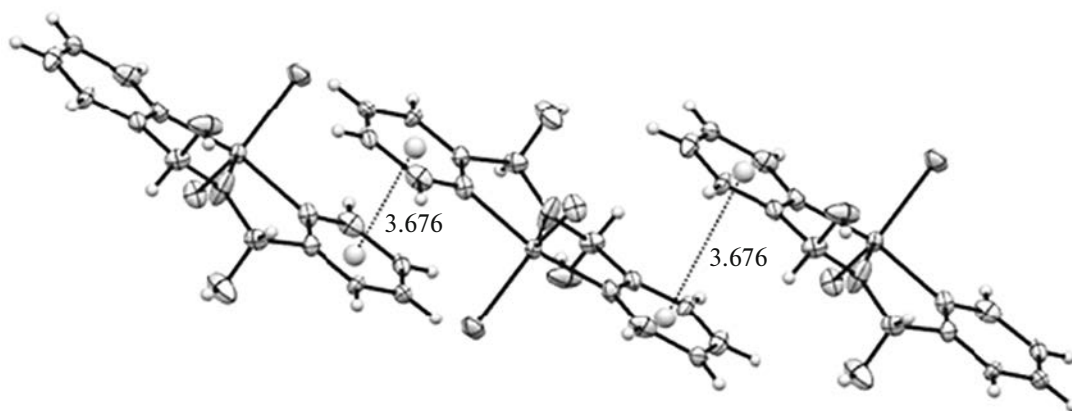


Fig. 4. Fragment of crystal structure II with π – π -stacking interaction between pyridine rings of neighboring chains.

carbonyl \leftrightarrow hem-diol shifts to the hem-diol. It is worth noting that in the absence of the zinc ion, the ratio of aldehyde and hem-diol forms is 2 : 1.

As compared with the spectrum of starting pyridine-2-carbaldehyde, in the ^1H NMR spectrum of complex **II** (Table 4) all signals shift noticeably to weak fields. This indicates that complexes with coordination through the pyridine nitrogen atom and the oxygen atom of the carbonyl or hem-diol group are formed in solutions.

Despite the general nature of transformations of the aldehyde group, an easy hydration of free pyridine-2-carbaldehyde [21], and a number of studies devoted to the acetalization of pyridine-2-carbaldehyde coordinated by metals [3–5, 9–11], complexes of the type considered here have not been reported.

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REFERENCES

1. A. Kleemann, J. Engel, B. Kutscher, and D. Reichert, *Pharmaceutical Substances: Syntheses, Patents, Applications of the Most Relevant APIs* (Thieme, Stuttgart/New York, 2008).
2. C. M. Alvarez, R. García-Rodríguez, and D. Miguel, *J. Chem. Soc., Dalton Trans.*, 3546 (2007).
3. W. Wang, B. Springler, and R. Alberto, *Inorg. Chim. Acta* **355**, 386 (2003).
4. G. Annibale, G. Marangoni, B. Pitteri, et al., *Trans. Met. Chem.* **25**, 485 (2000).
5. V. Bertolasi, G. Annibale, G. Marangoni, et al., *J. Coord. Chem.* **56**, 397 (2003).
6. V. E. Alvarez, R. J. Allen, T. Matsubara, and P. C. Ford, *J. Am. Chem. Soc.* **96**, 7686 (1974).
7. A. E. El-Hilaly and M. S. El-Ezaby, *J. Inorg. Nucl. Chem.* **38**, 1533 (1976).
8. R. H. Prince and P. Wyeth, *J. Inorg. Nucl. Chem.* **43**, 845 (1981).
9. A. M. Guidote, K.-I. Ando, Y. Kurusu, et al., *Inorg. Chim. Acta* **314**, 27 (2001).
10. M. G. B. Drew, S. Nag, P. K. Pal, and D. Datta, *Inorg. Chim. Acta* **361**, 2562 (2008).
11. K. C. Mondal, O. Sengupta, and P. S. Mukherjee, *Inorg. Chem. Commun.* **12**, 682 (2009).
12. K. J. Franz, *Curr. Opin. Chem. Biol.* **17**, 143 (2013).
13. R. H. Prince, *J. Inorg. Nucl. Chem.* **43**, 839 (1981).
14. B. Müller and H. Vahrenkamp, *Eur. J. Inorg. Chem.*, 137 (1999).
15. J.-L. Liu, Y.-C. Chen, Q.-W. Li, et al., *Chem. Commun.* **49**, 6549 (2013).
16. G. M. Sheldrick, *Acta Crystallogr., Sect. A* **64**, 112 (2008).
17. A. W. Addison, T. N. Rao, J. Reedijk, et al., *J. Chem. Soc., Dalton Trans.*, 1349 (1984).
18. J. M. Li, *Acta Crystallogr., Sect. E* **64**, m1468 (2008).
19. J. Emsley, *The Elements* (Clarendon Press, Oxford, 1991).
20. Y. Pocker and J. E. Meany, *J. Am. Chem. Soc.* **89**, 631 (1967).
21. Yu. M. Shapiro, *Russ Chem. Rev.* **60**, 1035 (1991). <https://doi.org/10.1070/RC1991v060n09ABEH001127>

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