

CRYSTAL STRUCTURE AND CHARACTERIZATION OF NEUTRAL COBALT(III) 2,3-PYRIDINEDICARBOXYLATE COMPLEX

Natalia Terenti^a, Marilena Ferbinteanu^b, Ana Lazarescu^{a*}

^aInstitute of Chemistry of Academy of Sciences of Moldova, 3, Academiei str., Chisinau MD-2028, Republic of Moldova
^bUniversity of Bucharest, 23, Dumbrova Rosie str., Bucharest 020462, Romania
*e-mail: analazarescu@yahoo.com

Abstract. A new Co(III) complex $[\text{Co}^{\text{III}}(2,3\text{-pdCH})_3] \cdot 3\text{H}_2\text{O}$, (2,3-pdcH₂ - 2,3-pyridinedicarboxylic acid) has been synthesized from a Co(II) salt at room temperature by using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as oxidant. The complex was characterized by elemental analysis, IR and UV-Vis spectroscopy, X-ray diffraction and thermogravimetric analyses. The complex crystallizes in the monoclinic space group $P2_1/c$. The crystal structure reveals a homoleptic complex with a distorted octahedral geometry, where the ligand acts as a monodeprotonated N, O-chelating anion.

Keywords: Co(III) complex, 2,3-pyridinedicarboxylic acid, thermal analysis, X-ray diffraction.

Received: 02 November 2017/ Revised final: 12 March 2018/ Accepted: 14 March 2018

Introduction

Cobalt and pyridinedicarboxylic acids are well known for their role in inorganic biochemistry [1,2]. Cobalt is an essential metal in proteins and plays major roles in a diverse range of enzymatic and electron-transfer processes due to its availability in two stable and accessible oxidation states, as other first-row transition metals. Co(III) ion is the active center of cobalamin, which is a vitamin with a key role in the normal functioning of the brain and nervous system, and the formation of red blood cells [3,4]. Furthermore, Co(III) complexes have been known long time among the most effective catalysts for the hydrolytic cleavage of amides, esters, and phosphates [5,6]. Several cobalt complexes possess anti-oxidant [7,8] and insulin-like effects [9,10], similar to vanadium complexes. On the other hand, the 2,3-pyridinedicarboxylic acid, being a polydentate carboxylic ligand, can act as a mono or double deprotonated form, generating a variety of coordination modes [11-13]. Quinolinic acid is well known for its important biological functions in the metabolism, such as enzyme inhibitor [1-3,14] plant membrane [15] and food sanitizer [16]. Also, pyridinedicarboxylic acids are found in the metabolic pathways of animals and they are used for the transport and scavenging of the metal ion by the body. All these properties have attracted the interest of scientific groups, not only in the field of coordination chemistry but also in inorganic and bioinorganic chemistry. It is

important to determine the crystal structure, composition and properties of various quinolinic metal complexes in the perspective to relate the effects of this metabolite and/or related compounds on physiological processes [17-19].

In continuation of our previous studies [20], we have synthesized a new Co(III) complex of composition $[\text{Co}(2,3\text{-pdCH})_3] \cdot 3\text{H}_2\text{O}$ (**1**) (where 2,3-pdcH is the monoanion of 2,3-pyridinedicarboxylic acid) in order to extend the knowledge on 2,3-pyridinedicarboxylate complexes in the system of Co(III) ion, to explore the possibility of its use as a model to explain some intricate reactions in biological systems and as monomeric blocks in the construction of supramolecular architectures.

Experimental part

Materials

The 2,3-pyridinedicarboxylic acid (2,3-pdcH₂) was purchased from Aldrich and the other chemicals were of analytical grade quality.

$[\text{Co}(2,3\text{-pdCH})_3] \cdot 3\text{H}_2\text{O}$ (**1**). A mixture of 2,3-pdcH₂ (1.5 mmol, 0.25 g) in 15 mL H₂O and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (2.5 mmol, 0.57g) in 10 mL H₂O was prepared. Further, it was added to an aqueous solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol, 0.14 g) in 10 mL. The solution turned dark violet upon mixing. The reaction mixture was left to crystallize slowly at room temperature. After two weeks, the solution was filtered to obtain small violet plates crystals large enough for

single-crystal X-ray studies. Yield: 45.0%. Calculated for $\{C_{21}H_{18}CoN_3O_{15}\}$: C 41.26, H 2.97, N 6.88%; Found: C 41.00, H 2.86, N 6.98%. IR bands (cm^{-1}): 3483, 3443, 3252, 3090, 3067, 2918, 2616, 2476, 2291, 1945, 1709, 1672, 1651, 1595, 1466, 1447, 1436, 1365, 1344, 1332, 1302, 1271, 1231, 1169, 1146, 1111, 1012, 996, 872, 828, 815, 758, 710, 690.

Measurements

The *infrared spectrum* was recorded in the ATR mode on a Perkin Elmer Spectrum 100 FT-IR Spectrometer in the range 4000-650 cm^{-1} . The *UV-Vis spectrum* was recorded for the aqueous solution of the complex with a Perkin Elmer UV-Vis spectrophotometer - Lambda 25 in the range of 900-200 nm. *Thermal analysis* (TG) was carried out in a Paulik-Paulik-Erdey derivatograph in the 20-1000°C range. The crucible containing 0.1 g sample was heated at 5°C·min⁻¹ in air. *Elemental analyses* (C, H, N) were carried out on an Elemental Analyzer Vario EL (III).

Crystal structure determination: A violet plate single crystal having dimensions of around 0.500 x 0.050 x 0.010 mm was mounted on a glass fiber. Crystallographic data for compound **1** were collected on a Rigaku R-AXIS RAPID II diffractometer with confocal monochromatized Mo-K α radiation, using ω - ϕ scan technique. The data were collected at a temperature of 20±1°C to a maximum 2 θ value of 55.0°. The structure was solved by direct methods [21] and refined anisotropically using a full-matrix least-squares method based on F^2 with the SHELX-97 [22]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the Crystal Structure [23] crystallographic software package except for refinement, which was performed using SHELXL97 [22]. The details of the crystal parameters, data collection and refinements for the complexes are presented in the section Results and discussion. Other details for the structural analysis are presented in the Supplementary Material file. CCDC 1581718 includes all supplementary crystallographic data of complex **1**. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion

In this article we studied the synthesis, structure and physico-chemical properties of a new 2,3-pyridinedicarboxylate complex of Co(III). A recent search in the

Cambridge Structural Data Base (CSD_2018) yielded about 28 cobalt compounds with 2,3-pyridinedicarboxylate moiety. From those, only 4 structures are Co(III) complexes [24-27] and neither one was a neutral and homoleptic complex. Herein, the complex **1**, named triaquatris(pyridine-3-carboxylic acid-2-carboxylato-O,N)-cobalt(III), has been isolated in the solid state and the structure has been assigned on the basis of its elemental analysis, IR and UV-Vis spectroscopy, single crystal X-ray diffraction study and thermogravimetric analysis.

Spectroscopic analyses

The typical vibrations of pyridine aromatic ring and the vibrational modes for carboxylic groups confirm the presence of the organic part ($\nu_{(C=C)} = 1595, 1564\text{ cm}^{-1}$; $\nu_{(C=N)} = 1466, 1447\text{ cm}^{-1}$, $\delta_{(C-O)} = 1111, 1012\text{ cm}^{-1}$) in the IR spectrum of the complex **1**. The spectrum reveals strong $\nu_{as}(\text{COO}^-)$ absorption bands at 1651, 1595 cm^{-1} and also $\nu_s(\text{COO}^-)$ absorption bands at 1466 and 1436 cm^{-1} . The presence of absorption band at 1709 cm^{-1} confirms the structural data indicating that one carboxylic group remains protonated. Comparison of the spectrum of **1** with the spectrum of the free ligand reveals broad absorption bands at 3483 and 3252 cm^{-1} , which are the characteristic peaks of $\nu_{as,s}(\text{OH})$ of the water molecules present in the complex [28].

The UV-Vis spectrum of complex **1** in water (Figure 1) displays weak absorptions at 375 and 522 nm, which are assigned to the ligand field transitions ${}^1A_{1g} \rightarrow {}^1T_{2g}$ and ${}^1A_{1g} \rightarrow {}^1T_{1g}$, respectively [29].

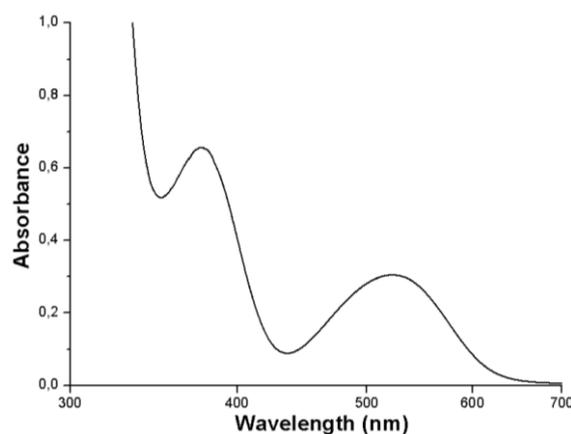


Figure 1. UV-Vis spectrum of the complex $[Co(2,3\text{-pdcH})_3] \cdot 3H_2O$ (**1**).

Crystal structure

Single-crystal X-ray study reveals that the asymmetric unit of complex **1** contains a mononuclear neutral complex with one cobalt ion, three 2,3-pyridinedicarboxylic anions and three

water molecules, $[\text{Co}(2,3\text{-pdcH})_3]\cdot 3\text{H}_2\text{O}$. The asymmetric unit with the atom numbering scheme is shown in Figure 2. The mononuclear complex crystallizes in the monoclinic space group $P2_1/c$. All crystallographic data and structure refinement for **1** are shown in Table 1. The Co(1) ion is coordinated by three 2,3-pyridinedicarboxylic anions that act as bidentate ligands. The charge of cobalt ion is +3. All ligands are monodeprotonated and form a distorted octahedral geometry with a $[\text{N}_3\text{O}_3]$ chromophore around cobalt(III) ion.

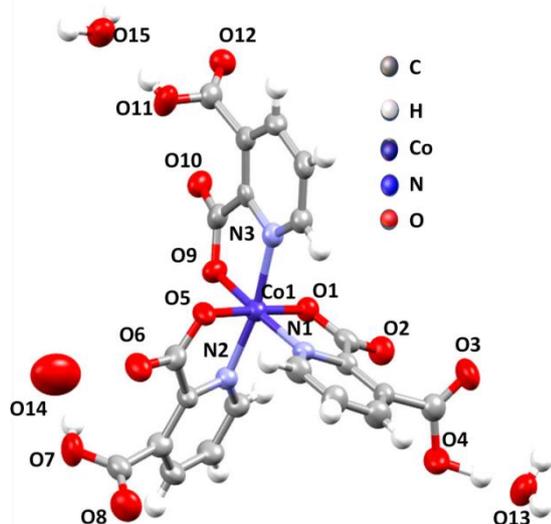


Figure 2. View of the asymmetric unit for $[\text{Co}(2,3\text{-pdcH})_3]\cdot 3\text{H}_2\text{O}$ with the atom numbering scheme (50% probability ellipsoid).

Each ligand coordinates in a chelate mode through the pyridine nitrogen atom and an oxygen atom from one deprotonated 2-carboxylic acid group, forming a five-membered chelate ring (Figure 2). The remaining protonated carboxylic group is not involved in coordination but forms intramolecular hydrogen bonds with three water molecules. From those three water molecules, one is disordered and for this reason, the hydrogen atoms could not be localized. The longest axis is formed by two Co-N bonds, Co1-N2 and Co1-N3 with the lengths 1.908(6) Å and 1.955(6) Å, the shortest axis is formed by two bonds Co1-O5 and

Co1-O1 (1.909(5) and 1.887(5) Å) and the third axis is formed by Co1-N1 and Co1-O9 bonds (1.929(7) and 1.875(6) Å), according to the data shown in Tables 2 and 3. The crystal packing reveals π - π stacking interactions between the pyridine rings of the ligand belonging to neighbour complex units in a parallel displaced mode (Figure 3), as well as an extended hydrogen bond network formed by the water molecules and non-coordinated carboxylic groups (Figure 4). The average bond distances M-O, M-N are similar to those in other 2,*n*-pyridinedicarboxylate cobalt complexes types of $[\text{Co}(2,3\text{-pdcH})_2(\text{N}_3)_2][\text{Na}_3(\text{H}_2\text{O})_{10}]$ [24], $[\text{Co}(2,3\text{-pdcH})_2(\text{en})_2][\text{Co}(\text{H}_2\text{O})_6]$ (where *en* is the ethylenediamine) [25].

Table 1

Crystallographic data and structure refinement for $[\text{Co}(2,3\text{-pdcH})_3]\cdot 3\text{H}_2\text{O}$ (1).

Parameter	Value
Empirical formula	$\text{C}_{21}\text{H}_{18}\text{CoN}_3\text{O}_{15}$
Formula weight, g/mol	611.32
Temperature, K	293
Crystal system	monoclinic
Space group	$P2_1/c$ (#14)
Lattice parameters	
<i>a</i> , Å	15.68(2)
<i>b</i> , Å	7.630(10)
<i>c</i> , Å	21.49(3)
β , °	110.54(5)
<i>V</i> , Å ³	2408(6)
<i>Z</i>	4
ρ_{calc} , g/cm ³	1.686
μ , cm ⁻¹	7.991
<i>F</i> (000)	1248.00
Radiation	MoK α
	($\lambda = 0.71075$ Å)
Reflections collected	7948
Independent reflections	4272
Data/restraints/parameters	4272/0/393
Goodness-of-fit on <i>F</i> ²	1.111
Final R indexes [<i>I</i> > 2 σ (<i>I</i>)]	0.0822
Final R indexes [all data]	0.1752
Largest diff. peak/hole, e Å ⁻³	0.45

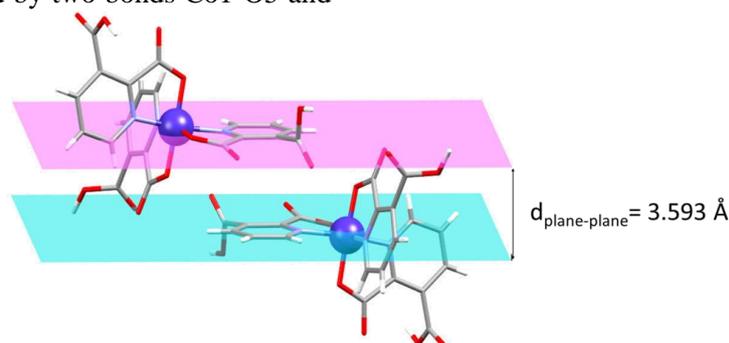


Figure 3. Crystal packing details showing the intermolecular π - π stacking interactions.

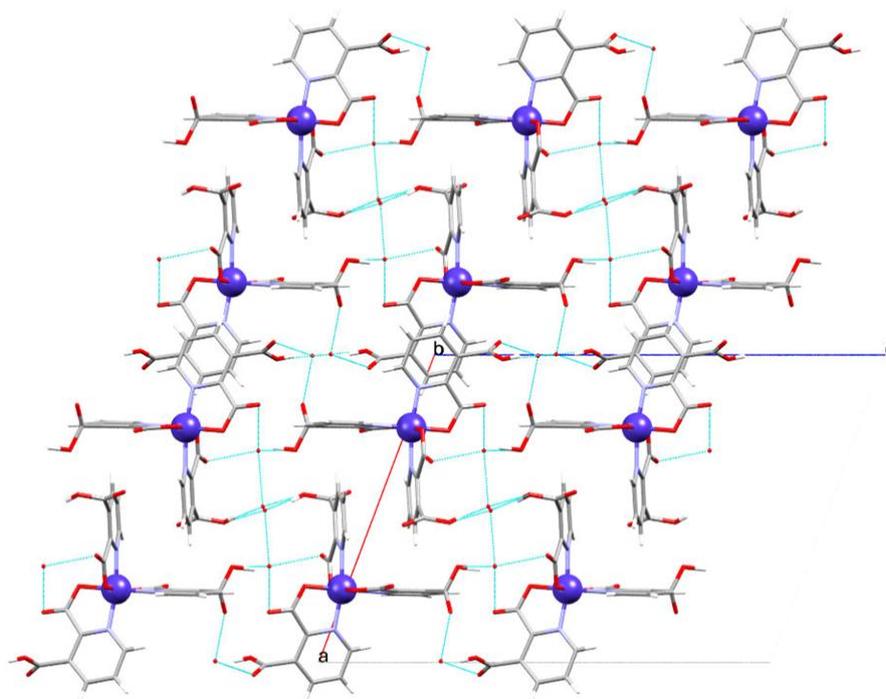


Figure 4. Crystal packing details showing the H-bonding network formed between the complex and water molecules.

Selected bond lengths (Å) for
[Co(2,3-pdcH)₃]·3H₂O (1).

Bond	<i>d</i> (Å)	Bond	<i>d</i> (Å)
Co1-O1	1.887(5)	Co1-O5	1.909(5)
Co1-O9	1.875(6)	Co1-N1	1.929(7)
Co1-N2	1.908(6)	Co1-N3	1.955(6)

Table 2

Selected bond angles (°) for
[Co(2,3-pdcH)₃]·3H₂O (1).

Angle	ω (°)	Angle	ω (°)
O1-Co1-O5	178.0(3)	O1-Co1-O9	89.1(2)
O1-Co1-N1	84.6(3)	O1-Co1-N2	93.5(2)
O1-Co1-N3	93.8(2)	O5-Co1-O9	92.2(2)
O5-Co1-N1	94.0(3)	O5-Co1-N2	85.1(2)
O5-Co1-N3	87.7(2)	O9-Co1-N1	173.7(2)
O9-Co1-N2	86.5(3)	O9-Co1-N3	85.3(3)
N1-Co1-N2	93.0(3)	N1-Co1-N3	95.9(3)
N2-Co1-N3	168.9(3)	Co1-O1-C1	115.5(5)
Co1-O5-C8	113.7(5)	Co1-O9-C15	114.6(4)
Co1-N1-C2	111.8(5)	Co1-N1-C6	128.1(6)
Co1-N2-C13	128.1(5)	Co1-N2-C9	113.4(5)
Co1-N3-C16	109.8(4)	Co1-N3-C20	130.0(6)

Table 3

Thermal studies

The thermal stability of the complex [Co(2,3-pdcH)₃]·3H₂O (**1**) was studied in the 20-1000°C temperature range and the results are presented in Figure 5. The TG, DTG curves of **1** exhibit three main distinct decomposition steps. In the 20-100°C temperature range the DTA curve shows one endothermic effect (I: 22-97.8°C peak

(8.73%)) which corresponds to the consecutive loss of three crystallization water molecules. An essential mass loss can be observed from the next decomposition step (II: 202-307°C peak (44.37%)), which is expressed in two overlapped processes accompanied by an exothermic effect in the DTA curve and corresponds to breaking and burning of one and a half of 2,3-pyridinedicarboxylic ligand. In the last step (III: 307-451°C peak (33.90%)), the remaining part of carboxylic ligands is eliminated, followed by a summary exothermic effect, well delimited on the DTG curve as two overlapped processes. The final decomposition temperature of complex **1** is 430°C with the residue of 13.10%. Therefore, the chemical and structural composition is in agreement with thermal analyses data.

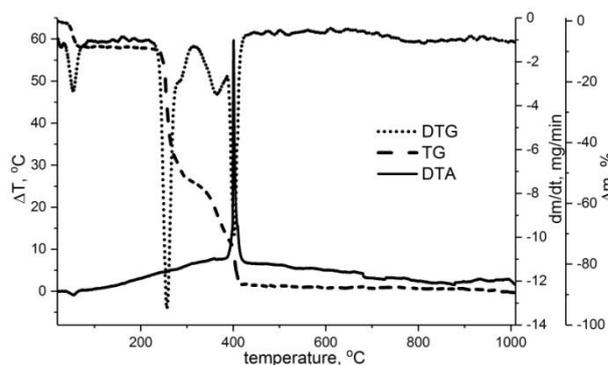


Figure 5. TG, DTG and DTA curves for the complex **1**.

Conclusions

The complex $[\text{Co}^{\text{III}}(2,3\text{-pdCH})_3]\cdot 3\text{H}_2\text{O}$ was obtained using a Co(II) salt and 2,3-pyridinedicarboxylic acid as precursors and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as the oxidant. The mononuclear complex crystallizes in the monoclinic space group $P2_1/c$. The 2,3-pyridinedicarboxylic ligand coordinates in a bidentate, chelate mode through the pyridine nitrogen atom and oxygen atom of the mono deprotonated 2-carboxylic group. Thermogravimetric analysis shows three main distinct decomposition steps and the final decomposition temperature of the complex is 430°C.

Supplementary information

Supplementary data are available free of charge at <http://ejm.asm.md> as PDF file.

References

- Cotton, F.A.; Wilkinson, G.; Murillo, C.A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed., John Wiley & Sons: New York, 1999, pp. 814-835. <https://www.wiley.com>
- Adams, H.; Shongwe, M.S.; Al-Bahri, I.; Al-Busaidi, E.; Morris, M.J. Bis[(2-pyridyl)(2-pyridylamino)methanolato]cobalt(III) perchlorate: a consequence of cobalt ion-assisted oxidative deamination of a tris(pyridyl)aminal ligand. *Acta Crystallographica*, 2005, C61, pp. m497-m500. DOI: <https://doi.org/10.1107/S0108270105033913>
- Khandar, A.; Shaabani, B.; Belaj, F.; Bakhtiari, A. Synthesis, characterization, electrochemical and spectroscopic investigation of cobalt(III) Schiff base complexes with axial amine ligands: the layered crystal structure of $[\text{Co}^{\text{III}}(\text{salophen})(4\text{-picoline})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2$. *Inorganica Chimica Acta*, 2007, 360(10), pp. 3255-3264. DOI: <https://doi.org/10.1016/j.ica.2007.03.036>
- Zhang, Y.L.; Ruan, W.L.; Zhao, X.J.; Wang H.G.; Zhu, Z.A. Synthesis and characterization of axial coordination cobalt(III) complexes containing chiral Salen ligands. *Polyhedron*, 2003, 22(12), pp. 1535-1545. DOI: [https://doi:10.1016/S0277-5387\(03\)00261-4](https://doi:10.1016/S0277-5387(03)00261-4)
- Tafesse, F.; Massoud, S.S.; Milburn, R.M. Amine ligand effects in hydroxoquatetraaminocobalt (III) ion promoted hydrolysis of adenosine 5'-triphosphate. *Inorganic Chemistry*, 1993, 32(9), pp. 1864-1865. DOI: [10.1021/ic00061a053](https://doi.org/10.1021/ic00061a053)
- Papavassiliou, A.G. Chemical nucleases as probes for studying DNA – protein interactions. *Biochemical Journal*, 1995, 305(Pt 2), pp. 345-357. <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC1136367/>
- Dimiza, F.; Papadopoulos, A.N.; Tangoulis, V.; Psycharis, V.; Raptopoulou, C.P.; Kessissoglou, D.P.; Psomas, G. Biological evaluation of cobalt(II) complexes with non-steroidal anti-inflammatory drug naproxen. *Journal of Inorganic Biochemistry*, 2012, 107(1), pp. 54-64. DOI: <https://doi.org/10.1016/j.jinorgbio.2011.10.014>
- Miodragovic, D.U.; Bogdanovic, G.A.; Miodragovic, Z.M.; Radulovic, M.D.; Novakovic, S.B.; Kaluderovic, G.N.; Kozlowski, H. Interesting coordination abilities of antiulcer drug famotidine and antimicrobial activity of drug and its cobalt(III) complex. *Journal of Inorganic Biochemistry*, 2006, 100(9), pp. 1568-1574. DOI: <https://doi.org/10.1016/j.jinorgbio.2006.05.009>
- Shalash, A.M.; Abu Ali, H.I. Synthesis, crystallographic, spectroscopic studies and biological activity of new cobalt(II) complexes with bioactive mixed sulindac and nitrogen-donor ligands. *Chemistry Central Journal*, 2017, 11(1), pp. 1-11. DOI: <https://doi.org/10.1186/s13065-017-0268-2>
- Kurtzhals, P.; Kiehr, B.; Sorensen, A.R. The Cobalt(III)-insulin hexamer is a prolonged-acting insulin prodrug. *Journal of Pharmaceutical Sciences*, 1995, 84(10), pp. 1164-1168. DOI: [10.1002/jps.2600841006](https://doi.org/10.1002/jps.2600841006)
- Teo, P.; Andy Hor, T.S. Spacer directed metallo-supramolecular assemblies of pyridine carboxylates. *Coordination Chemistry Reviews*, 2011, 255(1-2), pp. 273-289. DOI: <https://doi.org/10.1016/j.ccr.2010.08.014>
- Semerci, F.; Yeşilel, O.Z.; Keskin, S.; Darcan, C.; Taş, M.; Dal, H. Construction of homo- and heterometallic-pyridine-2,3-dicarboxylate metallosupramolecular networks with structural diversity: 1D T5(2) water tape and unexpected coordination mode of pyridine-2,3-dicarboxylate. *Crystal Engineering Communications*, 2013, 15(16), pp. 1244-1256. DOI: [10.1039/C2CE26675J](https://doi.org/10.1039/C2CE26675J)
- Wang, G.-H.; Li, Zh.-G.; Jia, H.-Q.; Hu, N.-H.; Xu, J.-W. Metal-organic frameworks based on the pyridine-2,3-dicarboxylate and a flexible bispyridyl ligand: syntheses, structures, and photoluminescence. *Crystal Engineering Communications*, 2009, 11(2), pp. 292-297. DOI: [10.1039/B809557D](https://doi.org/10.1039/B809557D)
- Slieman, T.A.; Nicholson, W.L. Role of dipicolinic acid in survival of *Bacillus subtilis* spores exposed to artificial and solar UV radiation. *Applied and Environmental Microbiology*, 2001, 67 (3), pp. 1274-1279. DOI: <https://doi.org/10.1128/AEM.67.3.1274-1279.2001>
- Errington, J. *Bacillus subtilis* sporulation: regulation of gene expression and control of morphogenesis. *Microbiological Reviews*, 1993, 57(1), pp. 1-33. <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC372899/>
- Murakami, K.; Tanemura, Y.; Yoshino, M. Dipicolinic acid prevents the copper-dependent oxidation of low density lipoprotein. *The Journal of Nutritional Biochemistry*, 2003, 14(2), pp. 99-103. DOI: [https://doi.org/10.1016/S0955-2863\(02\)00252-8](https://doi.org/10.1016/S0955-2863(02)00252-8)

17. Suga, T.; Okabe, N. Bis(pyridine-2,3-dicarboxylato-N,O)-copper(II). *Acta Crystallographica, Section C*, 1996, C52, pp. 1410-1412. DOI: <https://doi.org/10.1107/S0108270196001126>
18. Dharmalingam, S.; Yoon, S. Bis(4-aminopyridine){2,2'-[1,2-phenylenebis(nitrilo methanylylidene)]diphenolato}cobalt(III) nitrate. *Acta Crystallographica, Section E*, 2013, E69, pp. m495–m496. DOI: <http://dx.doi.org/10.1107/S1600536813020953>
19. Oliveira, C.G.; Maia, P.S.; Miyata, M.; Pavan, F.R.; Leite, C.Q.F.; Tonon de Almeida, E.; Deflon, V.M. Cobalt(III) complexes with thiosemicarbazones as potential anti-*Mycobacterium tuberculosis* agents. *Journal of Brazilian Chemical Society*, 2014, 25(10), pp. 1848-1856. DOI: <https://doi.org/10.5935/0103-5053.20140149>
20. Lazarescu, A.; Shova, S.; Bartolome, J.; Alonso, P.; Arauzo, A.; Balu, A.; Simonov, Yu.; Gdaniec, M.; Turta, C.; Filoti, G.; Luque, R. Heteronuclear (Co-Ca, Co-Ba) 2,3-pyridinedicarboxylate complexes: synthesis, structure and physico-chemical properties. *Dalton Transactions*, 2011, 40(2), pp. 463-471. DOI: <https://doi.org/10.1039/C0DT00858C>
21. Altomare, A.; Casciarano, G.; Giacovazzo, C.; Guagliardi, A. Completion and refinement of crystal structures with SIR92. *Journal of Applied Crystallography*, 1993, 26(3), pp. 343-350. DOI: <https://doi.org/10.1107/S0021889892010331>
22. Sheldrick, G.M. A short history of SHELX. *Acta Crystallographica*, 2008, A64, pp. 112-122. DOI: <http://dx.doi.org/10.1107/S0108767307043930>
23. Crystal Structure 4.2: Crystal Structure Analysis Package, Rigaku Corporation (2000-2015). Tokyo 196-8666, Japan. <https://www.rigaku.com>
24. Goher, M.A.S.; Youssef, A.A.; Mautner, F.A. Synthesis and structural characterization of two new anionic cobalt(III) azide complexes of 2,3- and 2,5-pyridine dicarboxylic acids. *Polyhedron*, 2006, 25(7), pp. 1531-1536. DOI: <https://doi.org/10.1016/j.poly.2005.10.014>
25. Colak, A.T.; Pamuk, G.; Yesilel, O.Z.; Yilmaz, F.; Buyukgungor, O. Hydrogen bonded supramolecular network from a mixed valence cobalt system: synthesis and crystal structure of [Co(H₂O)₆][Co(pydc)₂(en)]₂·14H₂O]. *Journal of Chemical Crystallography*, 2012, 42(1), pp. 76-82. DOI: <https://doi.org/10.1007/s10870-011-0206-4>
26. Mahata, P.; Sankar, G.; Madras, G.; Natarajan, S. A novel sheet 4f-3d mixed-metal pyridine dicarboxylate: synthesis, structure, photophysical properties and its transformation to a perovskite oxide. *Chemical Communications*, 2005, 0(46), pp. 5787-5789. DOI: [10.1039/b509588c](https://doi.org/10.1039/b509588c)
27. Natarajan, S.; Mandal, S.; Mahata, P.; Rao, V.K.; Ramaswamy, P.; Banerjee, A.; Paul, A.K.; Ramya, K.V. The use of hydrothermal methods in the synthesis of novel open-framework materials. *Journal of Chemical Science (Bangalore, India)*, 2006, 118(6), pp. 525-536. <http://www.ias.ac.in/listing/articles/jcsc/118/06>
28. Nakamoto, K. *Infrared spectra of inorganic and coordination compounds*. John Wiley and Sons: New York, 1991, 504 p. DOI: [10.1002/9780470405840](https://doi.org/10.1002/9780470405840)
29. Harris, D.; Bertolucci, M. *Symmetry and spectroscopy: an introduction to vibrational and electronic spectroscopy*. Dover Publication: New York, 1989, 550 p. <http://store.doverpublications.com/048666144x.html>