

# Synthesis and characterization of dipicolinic acid hydrazide derivative and Co(III) and Cr(III) complexes

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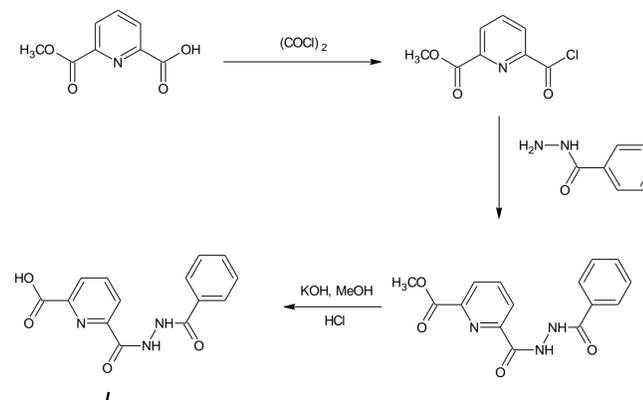
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**Introduction:** Derivatives of pyridine 2,6-dicarboxylic acid commonly coordinate to transition metals as partly or fully deprotonated ligands in a various coordination modes [1]. Dipicolinic acid hydrazide are interesting multidentate chelating systems, that can be used as pharmacologically active compounds because of their antibacterial and anti-inflammatory properties, amphophilic character and low toxicity [2]. This class of compounds contain a large number of potential donor atoms which are capable of coordinating to the metal centers in diverse arrangements. Picolinate and dipicolinate derivatives usually coordinate to transition metals in O,N,O chelating mode through the 2,6 pyridine dicarboxylate moiety. Herein we present synthetic procedures for obtaining two new complexes of biologically important metal ions, Co(III) and Cr(III), with dipicolinic acid hydrazide as N,O-donor ligand and diaminehexane as co-ligand.

**Syntheses and instrumental methods :** The dipicolinic acid hydrazide derivative 6-[[2-(phenylcarbonyl)hydrazino]carbonyl]pyridine-2-carboxylate (**L**) was prepared according to **Scheme 1**. The corresponding CoL and CrL complexes were prepared by reactions of L with Co(III) and Cr(III) chlorides with hexanediamine as co-ligand in methanol/dimethylformamide solvent system and ammonia as deprotonating agent.

IR spectra were recorded on Shimadzu FTIR 8400S spectrophotometer using the DRS 8000 attachment, in the 4000-400 cm<sup>-1</sup> region. Thermogravimetric analyses were performed using a simultaneous TGA-DSC analyser (Mettler-Toledo TGA/DSC 1). The single-crystal X-ray diffraction data were collected at 150 K and at room temperature on an Oxford Diffraction SuperNova CCD diffractometer with graphite-monochromated Mo-K<sub>α</sub> radiation (λ = 0.71073 Å) using ω-scans. Electrochemical experiments were performed on PalmSens potentiostat/galvanostat (PalmSens BV, Utrecht, The Netherlands) driven by PSTrace 1.2 software.

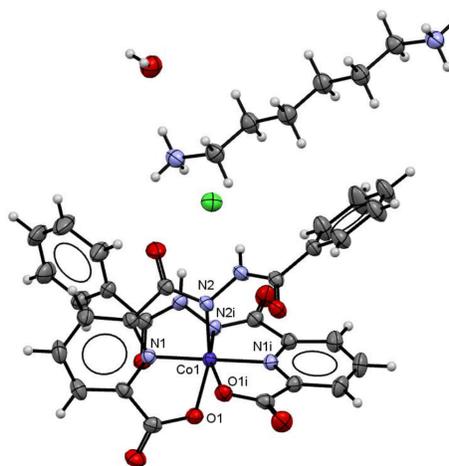


**Scheme 1.** The synthesis route for ligand L

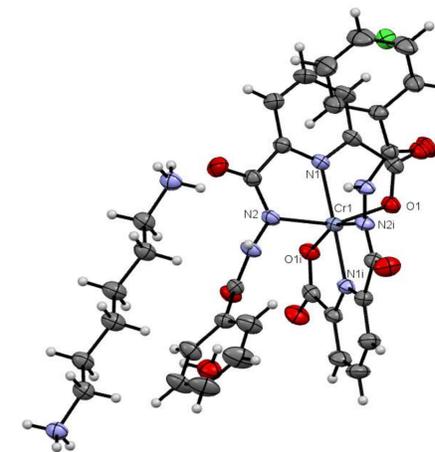
**Results and discussion:** The general and crystallographic data for the compounds are shown in Table 1, and the molecular composition on Figures 1 and 2. Both complexes crystallize in *C* 2/*c* monoclinic space group and have a similar coordination sphere. The metal M(III) ion is coordinated by two tridentate dipicolinate dianions in a distorted [M(N<sub>2</sub>O)<sub>2</sub>] octahedral geometry. These mixed ligand chelate complexes are isomorphs and contain metal ion coordinated by two deprotonated hydrazide nitrogen atoms and two oxygen atoms in equatorial plane. The axial coordination sites are occupied by two pyridyl nitrogen atoms. In the crystal structure of both complexes, the molecules are stabilized by intricate pattern of O-H...O, N-H...O and N-H...Cl hydrogen bond interactions which form an infinite three-dimensional supramolecular network. The hexanediamine cations connect two discrete complex compound molecules via strong N-H...O hydrogen bonds, approximately along -101 crystallographic directions. Thus connected molecules create supramolecular zig-zag motif (Fig. 3). The zig-zag structure is additionally stabilized by a series of N-H...Cl interactions that involve chlorine anion, hexanediamine cation and uncoordinated hydrazide nitrogen atom. Interestingly, crystal packing arrangement of CrL is almost identical as in CoL with some minor differences in hydrogen bond geometry. Therefore it can be concluded that the presence of different metal cation (Cr(III)) in this type of coordination compounds has an almost insignificant impact on crystal structure and that packing of molecules is driven by the presence of uncoordinated species in crystal structure (hexanediamine cation, water molecule and chlorine anion), which is well supported by hydrogen bonds patterning. The results of IR spectroscopy and thermal analyses are in a good agreement with crystal structure determination. Cyclic voltammogram of CoL complex (Fig. 4) showed one reduction peak at the potential, E<sub>p,c</sub> = 0.34 V, which correspond to reduction of Co<sup>3+</sup> ion to Co<sup>2+</sup> ion in CoL complex.

**Table 1.** Crystallographic data and structure refinement details

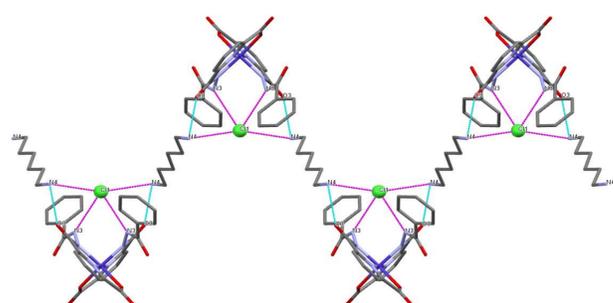
Compound	CoL	CrL
Formula	C <sub>34</sub> H <sub>40</sub> ClCoN <sub>8</sub> O <sub>10</sub>	C <sub>34</sub> H <sub>40</sub> ClCrN <sub>8</sub> O <sub>10</sub>
Formula weight	815.12	808.19
crystal system	monoclinic	monoclinic
space group	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
T, (K)	150(2)	296(2)
a (Å)	12.124(5)	12.2042(3)
b (Å)	17.905(5)	17.7978(4)
c (Å)	16.677(5)	16.6565(4)
β/ °	91.768(5)°	91.654(2)
V/Å <sup>3</sup>	3619(2)	3616.42(15)
Z	4	4
D <sub>calc</sub> (g cm <sup>-3</sup> )	1.496	1.484
R <sub>1</sub> <sup>a</sup> , [F <sub>o</sub> ≥ 4σ(F <sub>o</sub> )]	0.0346	0.0359



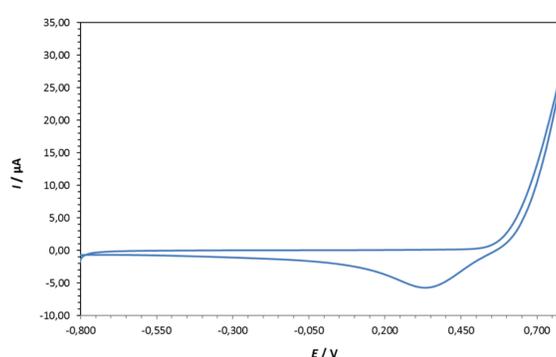
**Fig. 1.** ORTEP plot of CoL with displacement ellipsoids of non-hydrogen atoms drawn at 50 % probability level. (i) -x, -y, -z



**Fig. 2.** ORTEP plot of CrL with displacement ellipsoids of non-hydrogen atoms drawn at 50 % probability level. (i) -x, -y, -z



**Fig. 3.** Representation of zig-zag supramolecular motif in CoL (hydrogen atoms are omitted for clarity). N-H...O and N-H...Cl interactions are represented by light blue and magenta dashed lines, respectively.



**Fig. 4.** Cyclic voltammogram of CoL complex solution (c = 5·10<sup>-4</sup> mol dm<sup>-3</sup>) scanned at glassy carbon electrode (I<sub>c</sub> = 0,1 M LiCl in methanol). Scan rate, ν = 150 mV/s.

**Conclusions:** In this study we have determined crystal and molecular structure of two new Co(III) and Cr(III) complexes with dipicolinic acid hydrazide derivative (L) as ligand. The coordination environment, and crystal packing arrangement are almost identical in both complexes. The results of spectroscopic investigations, thermal analysis and cyclic voltammetry are in a good agreement with structural analyses.

## References:

- [1] H. M. Duy, I. Lee, S. Lee, H. Yoo, *Eur.J.Inorg.Chem.* (2017), 3736.
- [2] T. Kolesa-Dobravc, A. Meden, F. Perdih, *New J.Chem.* **39** (2015) 4265.