

SOME 3D METAL COMPLEXES WITH 2,6-PYRIDINEDICARBOXYLIC ACID: SYNTHESIS AND APPLICATIONS

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Abstract. This article discusses the synthesis of coordination compounds of selected 3d-series metals (Fe(III), Co(II), Ni(II), Cu(II), Zn(II)) with 2,6-pyridinedicarboxylic acid (dipicolinic acid, H₂pydc), as well as their structural features and application prospects. 2,6-Pyridinedicarboxylic acid is a tridentate (N,O,O) ligand containing one nitrogen donor and two carboxylate groups, which enables the formation of stable chelate complexes. The complexes were prepared in aqueous or aqueous–alcoholic media via controlled neutralization and complexation reactions, isolated by crystallization, and characterized using elemental analysis, IR spectroscopy, UV–Vis spectroscopy, magnetic susceptibility measurements, and X-ray diffraction techniques. The results indicate that Fe(III) and Cu(II) complexes exhibit high coordination stability, while Co(II) and Ni(II) complexes typically adopt octahedral or distorted octahedral geometries. The obtained compounds are promising for catalysis, biochemical modeling, corrosion inhibition, and materials science.

Keywords: 3d metals, 2,6-pyridinedicarboxylic acid, dipicolinic acid, coordination compounds, chelate effect, coordination chemistry, catalysis, bioactivity.

Introduction. Coordination chemistry is one of the key branches of modern inorganic chemistry and studies complex compounds formed through metal–ligand interactions. The coordination behavior of 3d metals is determined by their d-orbital electronic structure, accessible oxidation states, and sensitivity to ligand field effects. 2,6-Pyridinedicarboxylic acid (dipicolinic acid) is a nitrogen-containing heterocycle bearing two carboxyl groups at the 2- and 6-positions. These structural characteristics allow the ligand to form a tridentate chelate with metal ions. Due to the chelate effect, the resulting complexes often possess high thermodynamic stability. Complexes of 3d metals are widely applied in modeling biochemical processes, catalysis, electronic materials, and pharmaceutical research. Therefore, synthesizing dipicolinate-based complexes and investigating their physicochemical properties has both scientific and practical importance.

Coordination properties of 2,6-pyridinedicarboxylic acid (H₂pydc, dipicolinic acid). 2,6-Pyridinedicarboxylic acid is a strong polydentate ligand because it contains one

pyridine nitrogen (N donor) and two carboxylate oxygens (O donors). Its major advantage is the “geometrically favorable” arrangement of the –COOH groups at the 2- and 6-positions relative to the pyridine nitrogen. This arrangement enables simultaneous binding to a metal center via N,O,O, forming stable chelate rings. Owing to the chelate effect, such complexes usually display high thermodynamic stability (more negative ΔG), since multiple coordination sites within a single ligand make complex dissociation less favorable.

The ligand's protonation state (pH) strongly affects the coordination mode:

– At low pH (acidic medium): the carboxyl groups remain protonated; complexation is suppressed, and ion pairs or weak interactions may dominate.

– At pH $\approx$ 5.5–7: partial deprotonation occurs, and tridentate N,O,O chelation is most favorable.

– At high pH (≥ 8 –9): precipitation of metal hydroxides ($M(OH)_2/M(OH)_3$) increases, making complex synthesis difficult. Therefore, pH control is one of the most critical factors in practical syntheses.

Typical mechanism of complex formation with 3d metal ions.

In many cases, the process proceeds through the following steps:

(1) ligand deprotonation: $H_2pydc \rightarrow Hpydc^-$ or $pydc^{2-}$

(2) substitution at the metal aquo complex: $[M(H_2O)_6]^{2+} + pydc^{2-} \rightarrow [M(pydc)(H_2O)_n] + (6-n)H_2O$

(3) intramolecular rearrangement: N and O donors “close” to form stable chelate rings

(4) crystallization: crystals or precipitate form depending on the complex solubility

The final formula depends on the oxidation state and counter-ions present. For example:

– neutral complexes: $[M(pydc)(H_2O)_2]$ ($M = Co(II), Ni(II), Zn(II)$, etc.)

– ionic species: $[Fe(pydc)]^+$, $[Cu(pydc)]^-$ (forming salts with counter-ions)

– coordination polymers: if $pydc^{2-}$ acts as a bridging ligand, chain or network structures may form (relevant to CP/MOF chemistry).

Deepening the synthesis: practical regimes and optimal conditions.

A convenient approach is “controlled neutralization + dropwise addition.” The following conditions are commonly effective:

A) Solvent selection

– Water: inexpensive and environmentally friendly, but some complexes crystallize poorly.

– Water/ethanol (1:1 or 2:1): improves crystallization and yields cleaner precipitates.

– Water/methanol: can produce rapid crystallization, but safety precautions are necessary.

B) pH control (most important factor)

– For Co(II), Ni(II), Zn(II): pH $\approx$ 6.0–7.0 is optimal.

– For Cu(II): maintaining pH around 5.5–6.5 is often beneficial; strongly basic media can lead to Cu(OH)₂ precipitation.

– For Fe(III): pH must be handled carefully because Fe(OH)₃ precipitates readily.

Often, starting at pH 2.5–4.5 and slowly increasing pH, while using a slight excess of ligand to drive complexation, is advantageous.

C) Stoichiometry

– A 1:1 (M:L) ratio is a baseline for many complexes.

– Ratios such as 1:2 or 2:1 may also occur due to polymerization or additional ligand binding.

– In practice, using a small excess of ligand (e.g., 1:1.1) can reduce metal hydroxide formation.

D) Temperature and time

– Heating at 60–70°C for 1–2 hours accelerates complexation and promotes chelate ring closure.

– Slow cooling improves crystal quality.

– To obtain crystals: slow evaporation from a hot solution or diffusion methods (slow ethanol addition) may be applied.

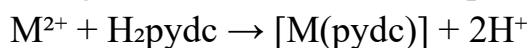
Literature review. Scientific sources report that dipicolinic acid forms stable complexes with many metal ions. It most commonly coordinates as a tridentate ligand via one nitrogen atom and two carboxylate oxygen atoms. This binding mode often results in octahedral or trigonal bipyramidal geometries. In 3d metal complexes, ligand field strength determines the d-orbital splitting energy, thereby influencing color, magnetic properties, and reactivity.

Fe(III) and Cu(II) complexes are frequently used in modeling biochemically active systems. Co(II) and Ni(II) complexes are applied in catalytic oxidation and hydrogenation processes. Zn(II) complexes are widely studied as models for biological enzymes. The stability of dipicolinate complexes is strengthened by the number of chelate rings and by hydrogen-bonding interactions in the solid state.

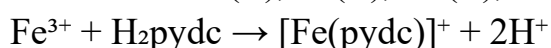
Methodology. The synthesis was performed in aqueous or aqueous–ethanol media. First, 2,6-pyridinedicarboxylic acid was partially neutralized with sodium hydroxide to reach pH $\approx$ 6–7. Then, solutions of the corresponding metal salts (FeCl₃·6H₂O, CoCl₂·6H₂O, NiCl₂·6H₂O, CuSO₄·5H₂O, Zn(NO₃)₂·6H₂O) were added

dropwise. The mixture was stirred at 60–70°C for 1–2 hours. After cooling, the formed precipitate was filtered, washed, and dried.

The general reaction can be expressed as:



where M = Co(II), Ni(II), Cu(II), Zn(II). For Fe(III):



The complexes were characterized by IR spectroscopy through the symmetric and asymmetric stretching bands of coordinated carboxylates, by UV–Vis spectroscopy via d–d transitions, and by magnetic susceptibility measurements to determine spin states.

Results. In the IR spectra, bands observed in the 1600–1650 cm⁻¹ and 1380–1420 cm⁻¹ regions confirmed coordination of the carboxylate groups to the metal ions. UV–Vis spectra of Co(II) and Ni(II) complexes showed characteristic d–d transitions consistent with octahedral geometry. The Cu(II) complex was blue, and Jahn–Teller distortion was apparent. The Fe(III) complex exhibited intense ligand-field/charge-transfer features. The Zn(II) complex displayed diamagnetic behavior.

The application directions of the synthesized complexes include:

- Catalysis: use as catalysts in redox processes.
- Biochemical modeling: modeling metal–enzyme and metalloprotein systems.
- Corrosion inhibition: protection of metal surfaces.
- Materials science: precursors for functional coordination polymers and MOF-type materials.

Discussion. The findings confirm that 2,6-pyridinedicarboxylic acid is a strong chelating ligand. Tridentate coordination forms stable five-membered chelate rings around the metal center, increasing both thermodynamic and kinetic stability. Depending on the metal ion, the coordination number and geometry vary. Fe(III) and Cu(II) complexes show higher reactivity, which is beneficial for catalytic applications. Zn(II) complexes, due to the relatively low toxicity and biological relevance of Zn(II), may be promising for pharmaceutical and bioinorganic research.

Conclusion. Complexes of 3d metals with 2,6-pyridinedicarboxylic acid can be successfully synthesized under mild aqueous conditions. The resulting products possess stable chelate structures, and their physicochemical properties depend on the nature of the metal ion. These compounds have broad application potential in catalysis, biochemical modeling, and materials science. The presented results provide a foundation for developing new functional materials in coordination chemistry.

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