

Preparation and Characterization of Zinc(II) Complexes with Coumalic Acid

Tea Kozić, Anamarija Stanković, Nikolina Filipović, Tomislav Balić
Department of Chemistry, University of Osijek, cara Hadrijana 8/a, 31 000 Osijek, Croatia
Presenting author: tkozic@kemija.unios.hr

INTRODUCTION & AIM

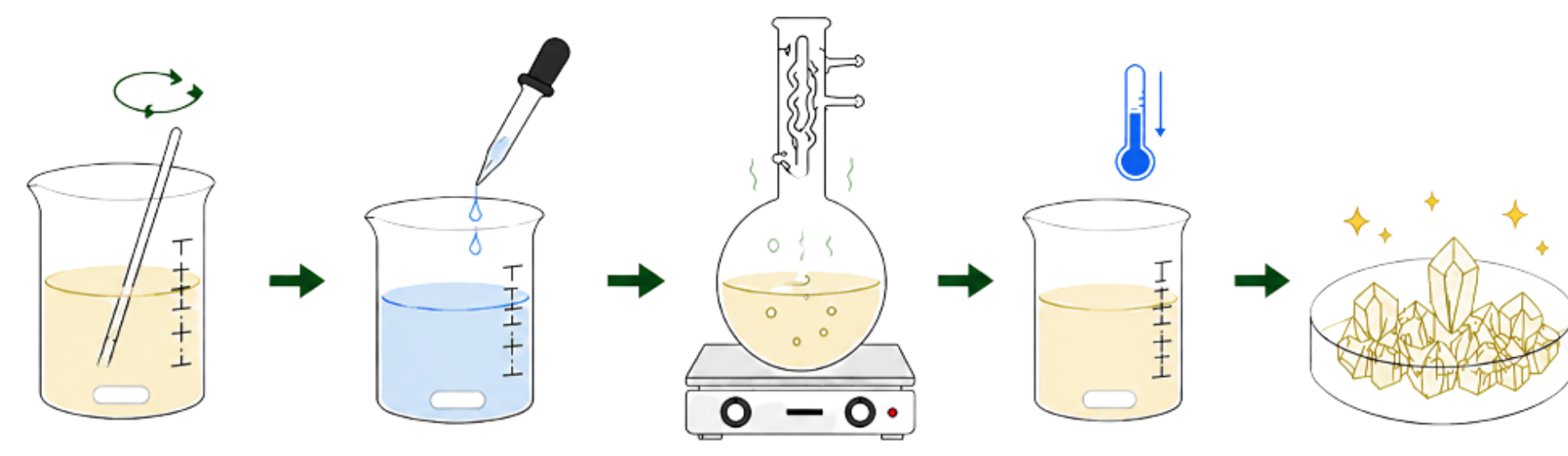
Hydroxypyranones are oxygen-containing heterocycles known for diverse coordination modes and biological activity. Due to adjacent carbonyl and hydroxyl groups, they readily form stable complexes with transition metal ions, making them attractive in coordination, medicinal, and materials chemistry. Their metal complexes exhibit antioxidant, antimicrobial, anticancer, and catalytic properties.

Coumalic acid (2-oxo-2H-pyran-5-carboxylic acid) is a versatile *O,O*-donor ligand that coordinates via carboxylate and carbonyl oxygens. Its conjugated pyranone ring enables electron delocalization and stabilizes various coordination geometries. It is also a valuable precursor for biologically relevant heterocycles.

Zinc(II) complexes are particularly important due to Zn^{2+} being d^{10} , non-redox-active, biocompatible, and low-toxic. Zinc compounds often show antimicrobial, antioxidant, and enzyme-modulating activity, serving as structural and functional models in bioinorganic chemistry.

Aim: To synthesize Zn(II) coumalate complexes using two different zinc salts—nitrate (K1) and acetate (K2) under mild conditions. To characterize them by FT-IR, PXRD, and TGA/DSC, and to understand how the choice of zinc precursor influences coordination mode and solid-state organization.

PREPARATION OF COMPLEXES



- Coumalic acid**
Coumalic acid (1 equiv.) is dissolved in a suitable solvent (ethanol/water mixture) with stirring.
- Zinc salt addition**
Zinc(II) acetate dihydrate (1 equiv.) or Zinc(II) nitrate hexahydrate (1 equiv.) is added to the solution under stirring.
- Heating under reflux**
The reaction mixture is heated under reflux at 60–80 °C for 2–4 hours with continuous stirring.
- Cooling**
The reaction mixture is allowed to cool to room temperature slowly.
- Product isolation**
White to pale yellow crystals of the zinc complex are formed and isolated by filtration, washed with cold water, and dried.

RESULTS & DISCUSSION

FT-IR spectroscopy

FT-IR analysis confirmed the formation of zinc(II) coumalate complexes K1 and K2. Significant spectral changes relative to the starting zinc salts and free coumalic acid indicate coordination of coumalate to Zn(II). Broad bands at 3200–3500 cm^{-1} are attributed to O–H stretching of water molecules and hydrogen bonding, while the absence of the characteristic carboxylic acid O–H band supports deprotonation of the –COOH group. Bands at 1600–1650 and 1380–1450 cm^{-1} correspond to asymmetric and symmetric COO^- stretching vibrations, confirming coordination of deprotonated carboxylate groups. The $\Delta\nu$ values (≈ 200 – 250 cm^{-1}) suggest a bridging or chelating bidentate coordination mode. Comparison of K1 and K2 revealed slight shifts in COO^- bands and differences in relative intensities, indicating that the zinc precursor (nitrate or acetate) influences the coordination environment and solid-state organization (Figure 1).

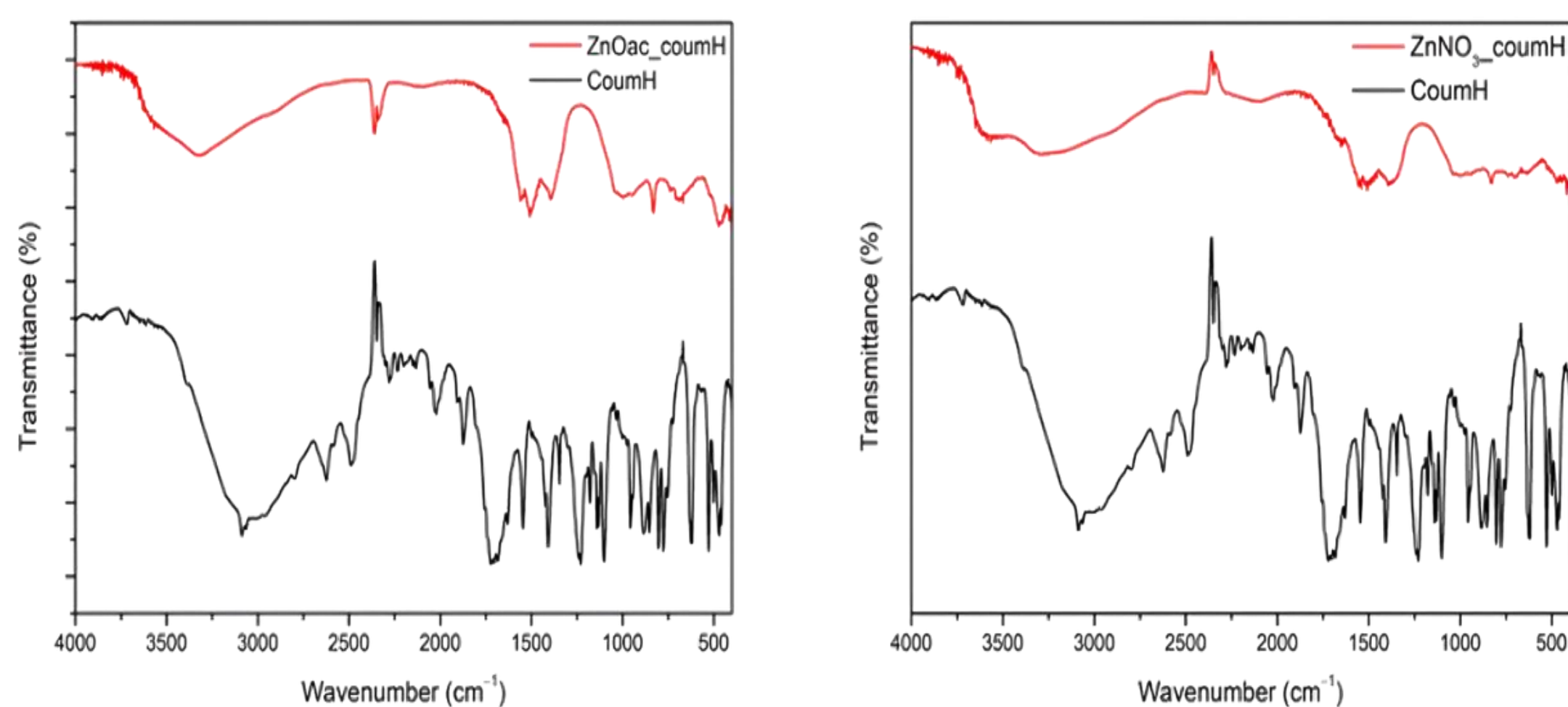


Figure 1. IR spectra of the pure ligand and Zn(II) complexes.

PXRD analysis

PXRD analysis confirmed that both synthetic procedures (K1 from $Zn(NO_3)_2$ and K2 from $Zn(OAc)_2$) produced crystalline zinc(II) coumalate complexes, as evidenced by sharp diffraction peaks. The main reflections at $2\theta \approx 12$ – 13° , 28 – 29° , and 33 – 34° indicate similar structural motifs in both compounds. However, differences in peak intensities and the presence of additional reflections suggest variations in crystal packing and structural organization, influenced by the zinc precursor. A broad background between 15 and 30° 2θ may indicate partial disorder or residual solvent effects. Both K1 and K2 contain deprotonated coumalate ligands with similar Zn–O bonding. FT-IR confirmed *O,O*-coordination, while PXRD revealed that the zinc precursor affects the final solid-state structure despite preserving the same fundamental metal–ligand interactions.

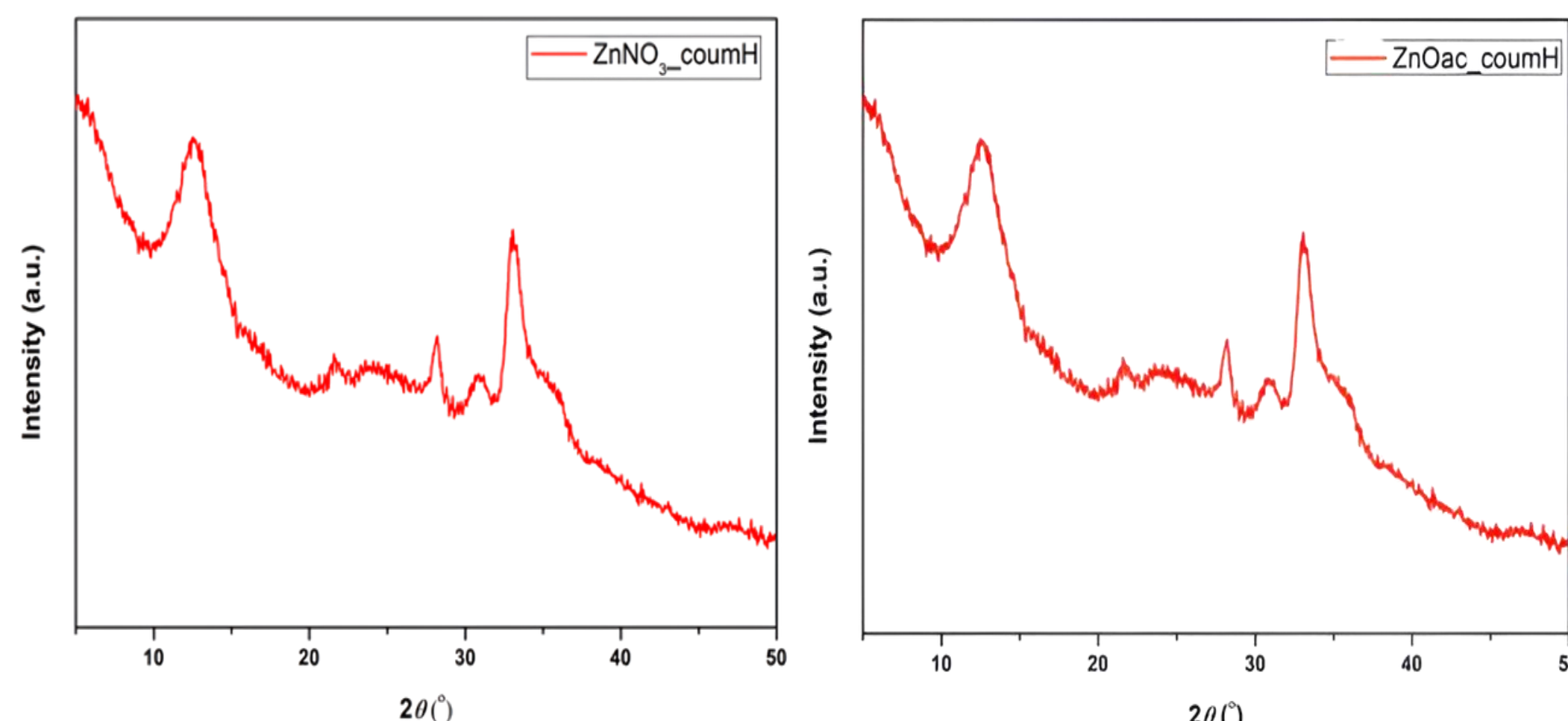


Figure 2. Powder X-ray diffraction (PXRD) patterns of $ZnNO_3$ _coumH (K1) and $ZnOAc$ _coumH (K2) complexes synthesized from zinc nitrate and zinc acetate.

POSSIBLE COMPLEX ARCHITECTURES

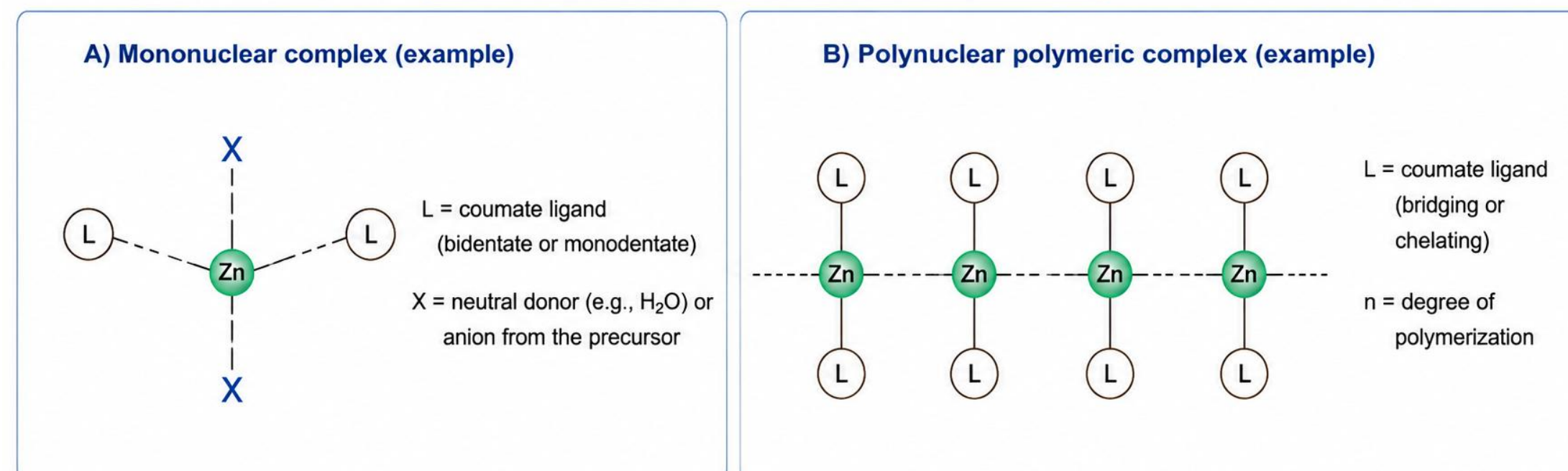


Figure 3. Possible coordination architectures of zinc(II) coumalate complexes: (A) mononuclear and (B) polymeric structures. Coumalate ligands may coordinate in chelating or bridging modes, leading to different solid-state arrangements.

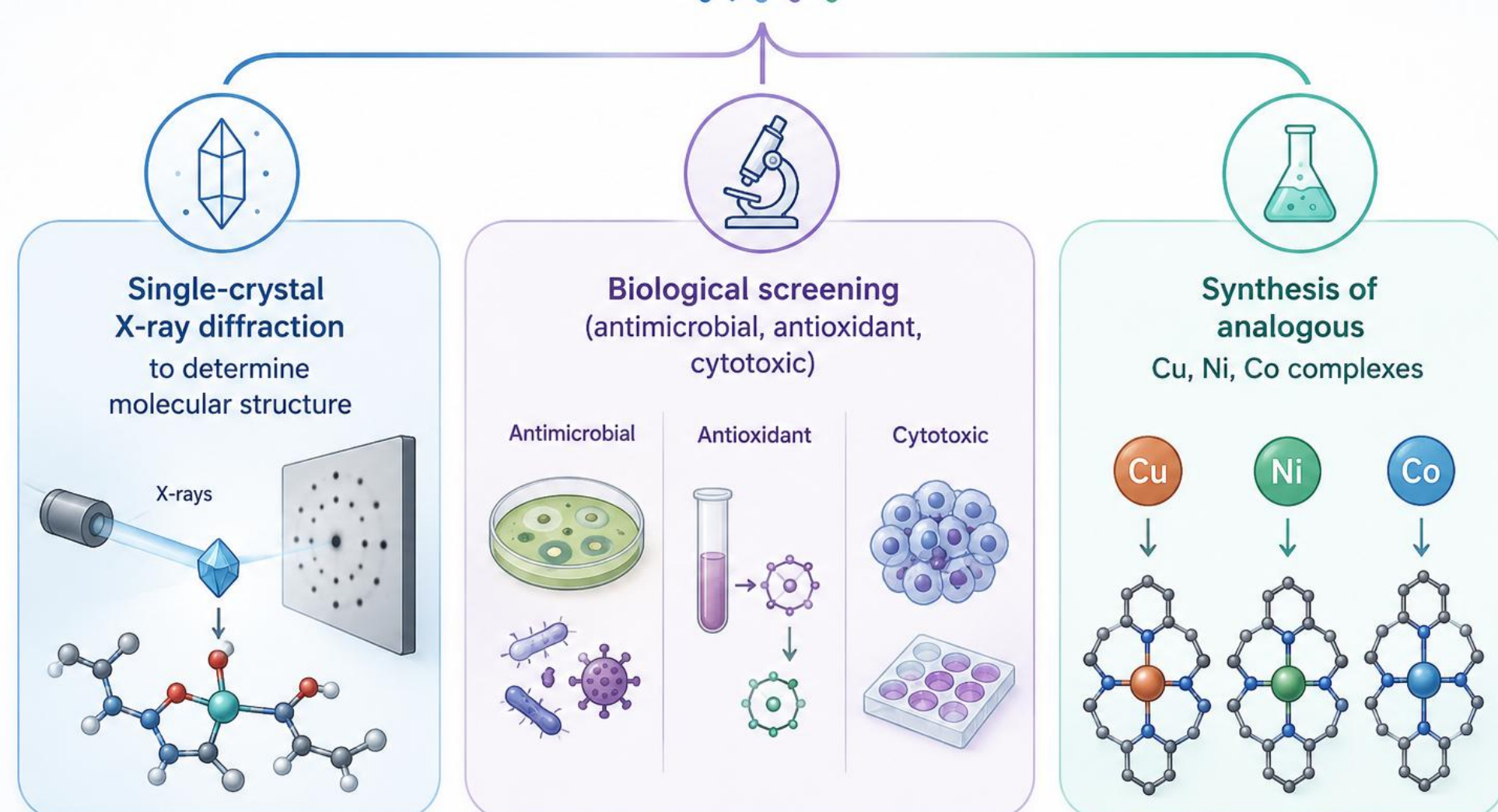
CONCLUSIONS

- Two new Zn(II) coumalate complexes (K1 from nitrate, K2 from acetate) were successfully synthesized
- FT-IR confirmed *O,O*-coordination of deprotonated coumalate to Zn(II). Spectral differences between K1 and K2 show that the zinc precursor influences the coordination environment
- PXRD revealed crystalline products with similar structural motifs but precursor-dependent crystal packing
- Both complexes are stable under ambient conditions and promising for bioinorganic and materials chemistry (e.g., antimicrobial, antioxidant studies)

References:

- Balić, T.; et al. (2022) Crystals, 12, 1234.
- Köse, D. A.; Öztürk, B.; Şahin, O.; Büyükgüngör, O. (2017) J. Therm. Anal. Calorim., 128, 1373–1383.
- Koç, S.; Kose, D. A.; Avci, E.; Kose, K. (2016) Hitit. J. Sci. Eng., 3, 15–22.

FUTURE PERSPECTIVES



Acknowledgment: The authors thank the Department of Chemistry, University of Osijek, for support and the central laboratory for FT-IR, PXRD, and TGA/DSC measurements.