

MALTOL AND KOJIC ACID AS VERSATILE O-DONOR LIGANDS IN TRANSITION METAL COMPLEXES

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INTRODUCTION

Hydroxypyranones, such as maltol and kojic acid, are versatile oxygen-donor ligands that readily form stable chelate rings with transition metals. While maltol typically acts as a classic bidentate *O,O*-donor, kojic acid exhibits more flexible coordination modes depending on the metal center and reaction conditions. Small variations in these ligand structures can significantly alter the geometry, thermal behavior, and overall physicochemical properties of the resulting complexes. In this work, a series of transition metal complexes containing maltol and kojic acid were synthesized under mild reaction conditions and characterized using complementary spectroscopic, thermal, electrochemical, and X-ray diffraction techniques (Fig. 1.). The study aimed to investigate metal–ligand interactions and the influence of ligand structure on the coordination and physicochemical properties of the synthesized complexes.^{1–3}

MATERIALS AND METHODES

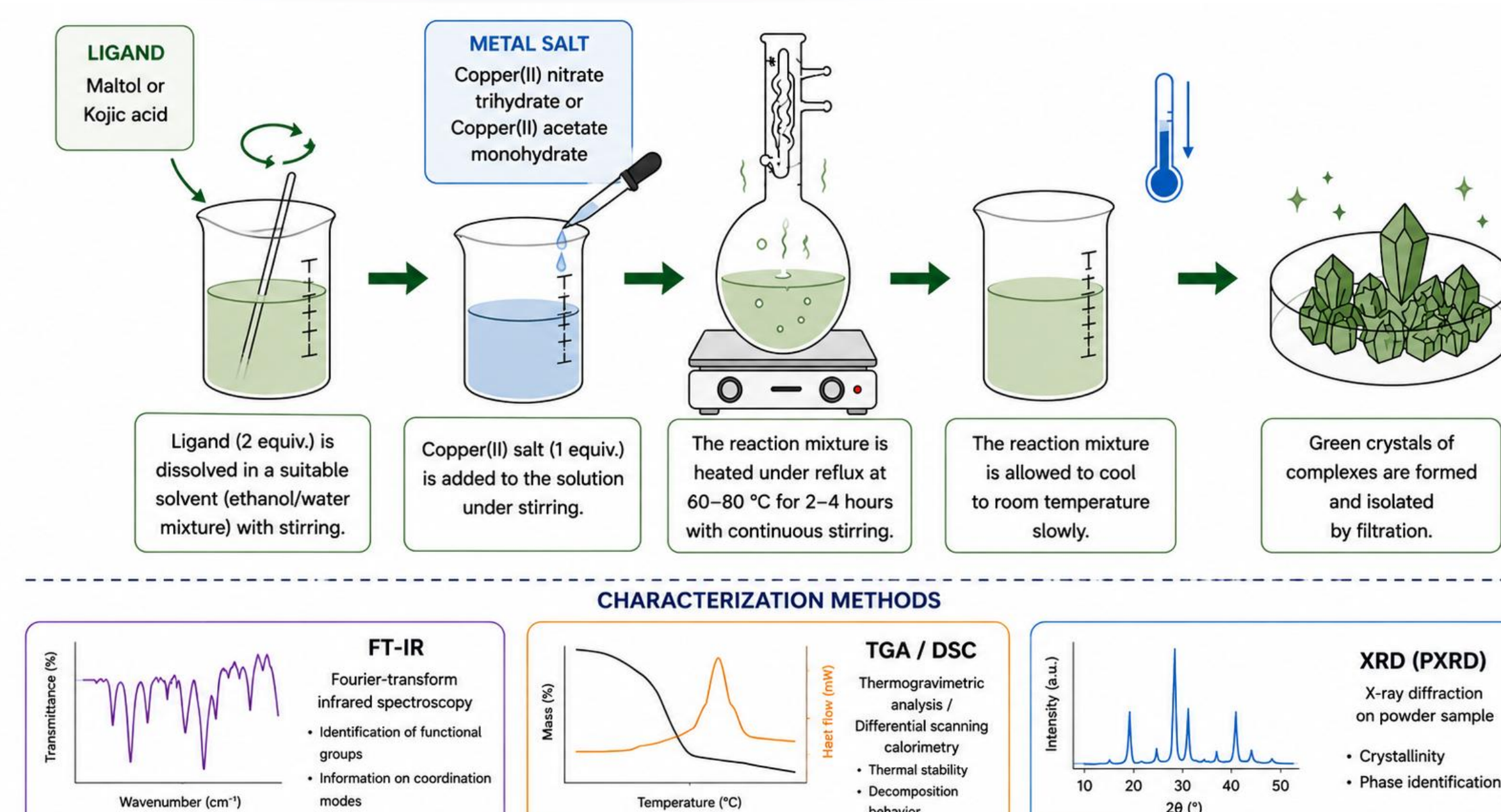


Figure 1. Preparation and Characterization Steps

RESULTS AND DISCUSSION

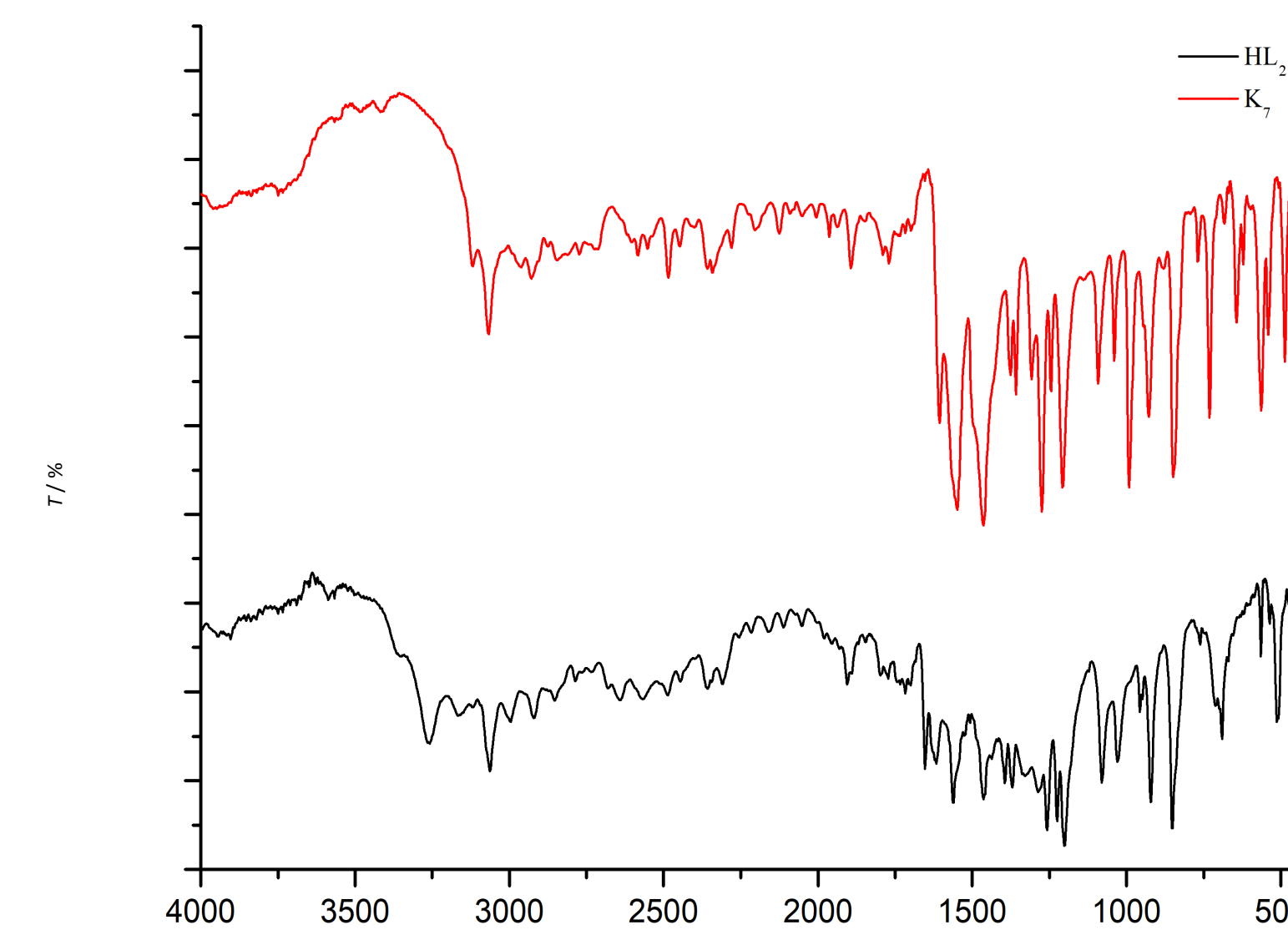
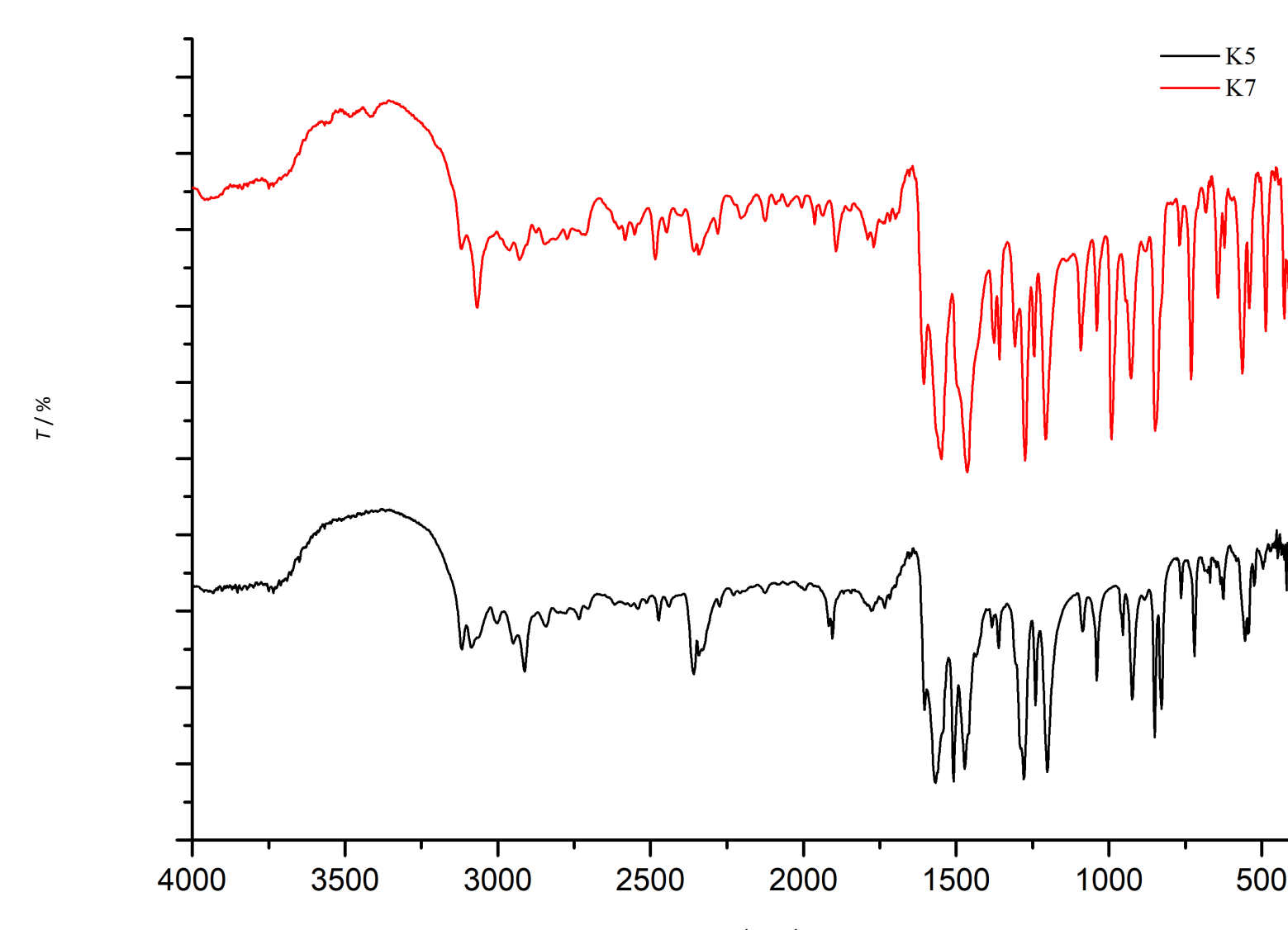
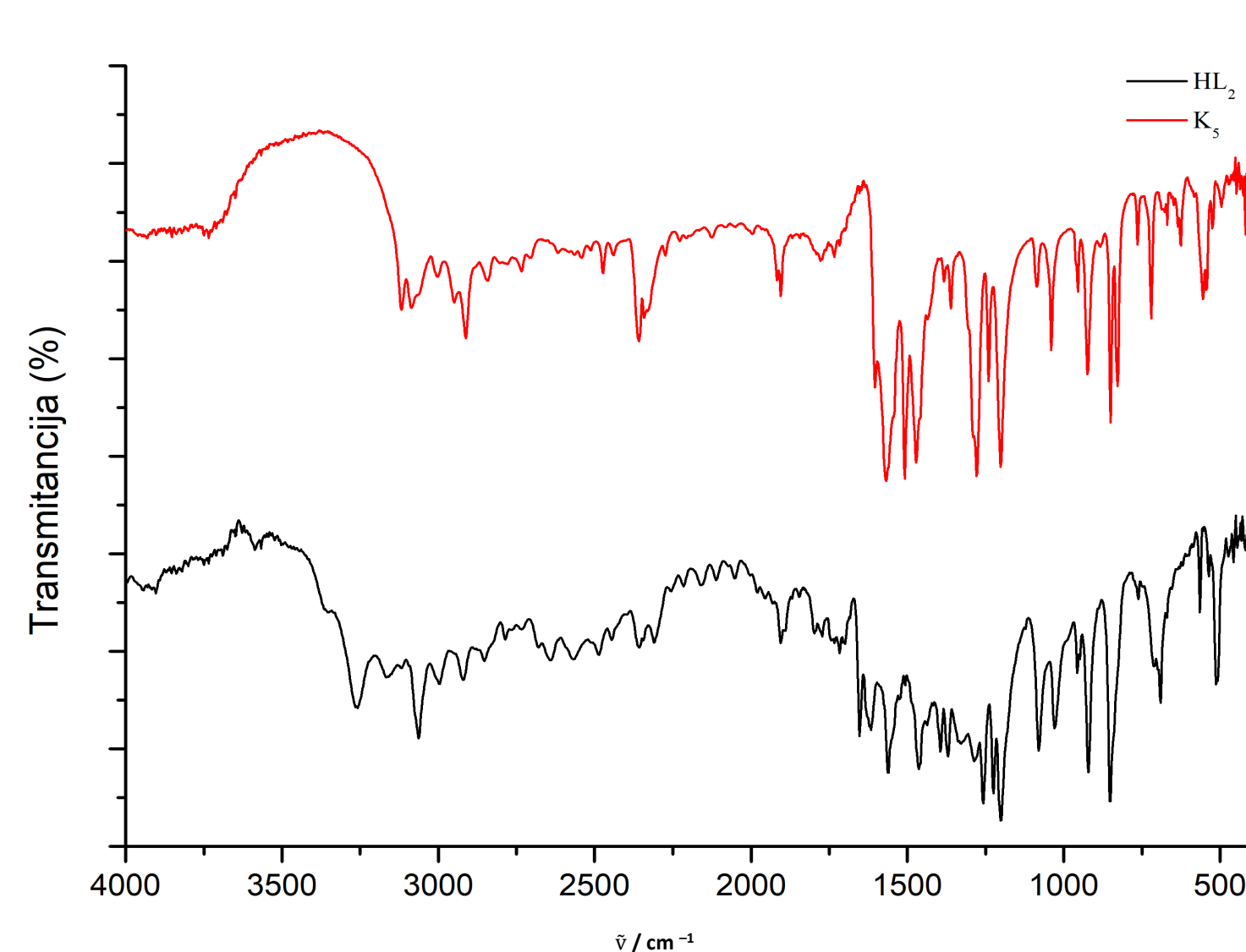


Figure 2. FT-IR Spectra Overlay of Maltol and Complexes K5 and K7

FT-IR and thermal analyses confirmed the formation of the metal–maltol complexes K5 and K7. For K5, the disappearance of the C–OH stretching band at 3255 cm^{−1} and the shift of the C=O band from 1616 to 1568 cm^{−1} indicate maltol deprotonation and bidentate *O,O*-coordination to Cu(II). A band at 719 cm^{−1} was attributed to Cu–O vibrations. In K7, maltol shows a similar coordination mode, while the characteristic band at 991 cm^{−1} confirms the presence of the V=O group (Fig. 2.).

Thermal analysis showed that K5 decomposes in one major step, with a mass loss of approximately 70% and a sharp exothermic DSC peak at 220 °C, leaving about 24% CuO residue. K7 decomposes in two steps within the 240–340 °C range, with mass losses of 20.61% and 50.76%, leaving approximately 30% residue attributed to V₂O₅ (Fig. 3). Overall, the results support the formation of stable complexes in which maltol acts as a bidentate *O,O*-donor ligand.

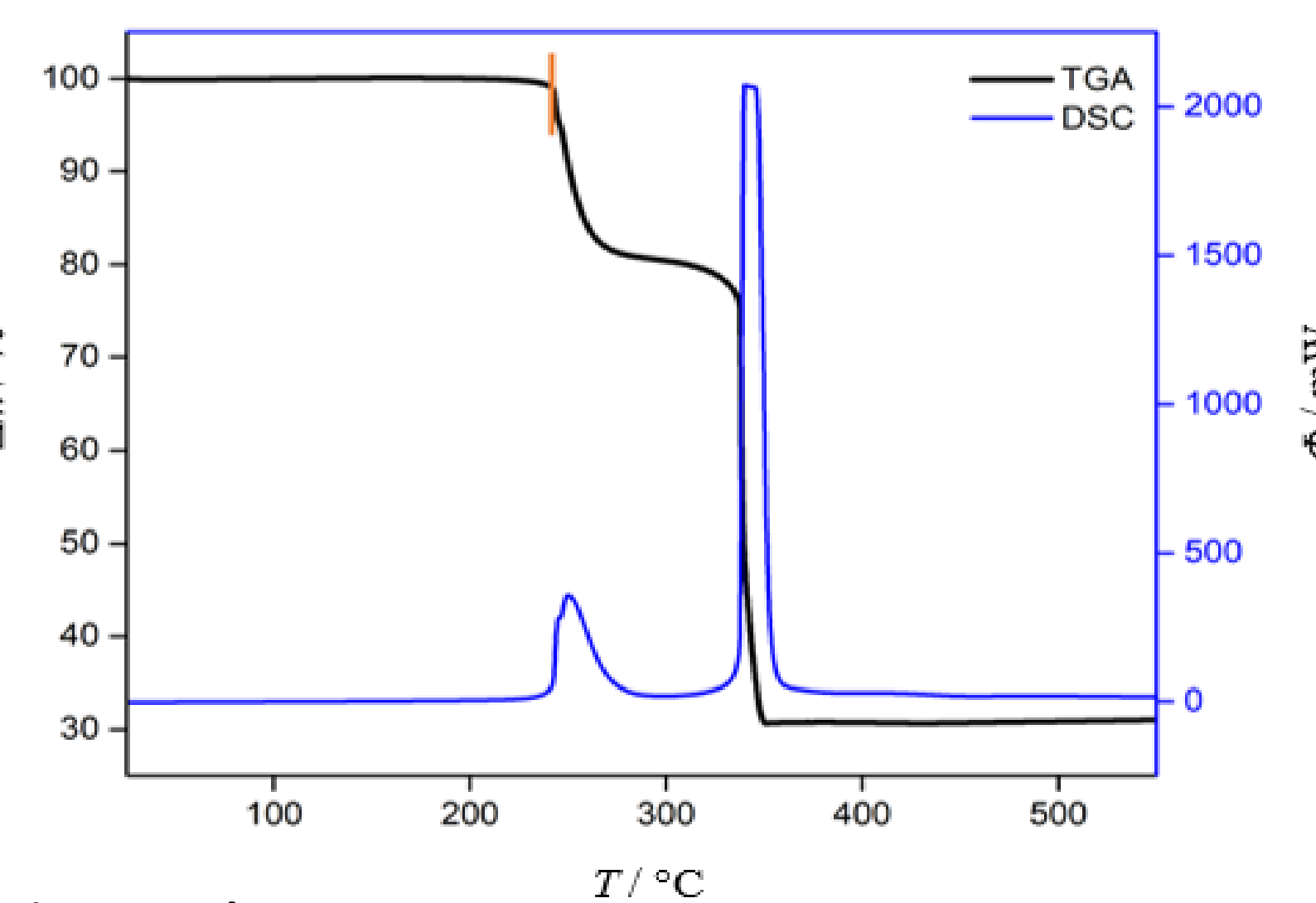
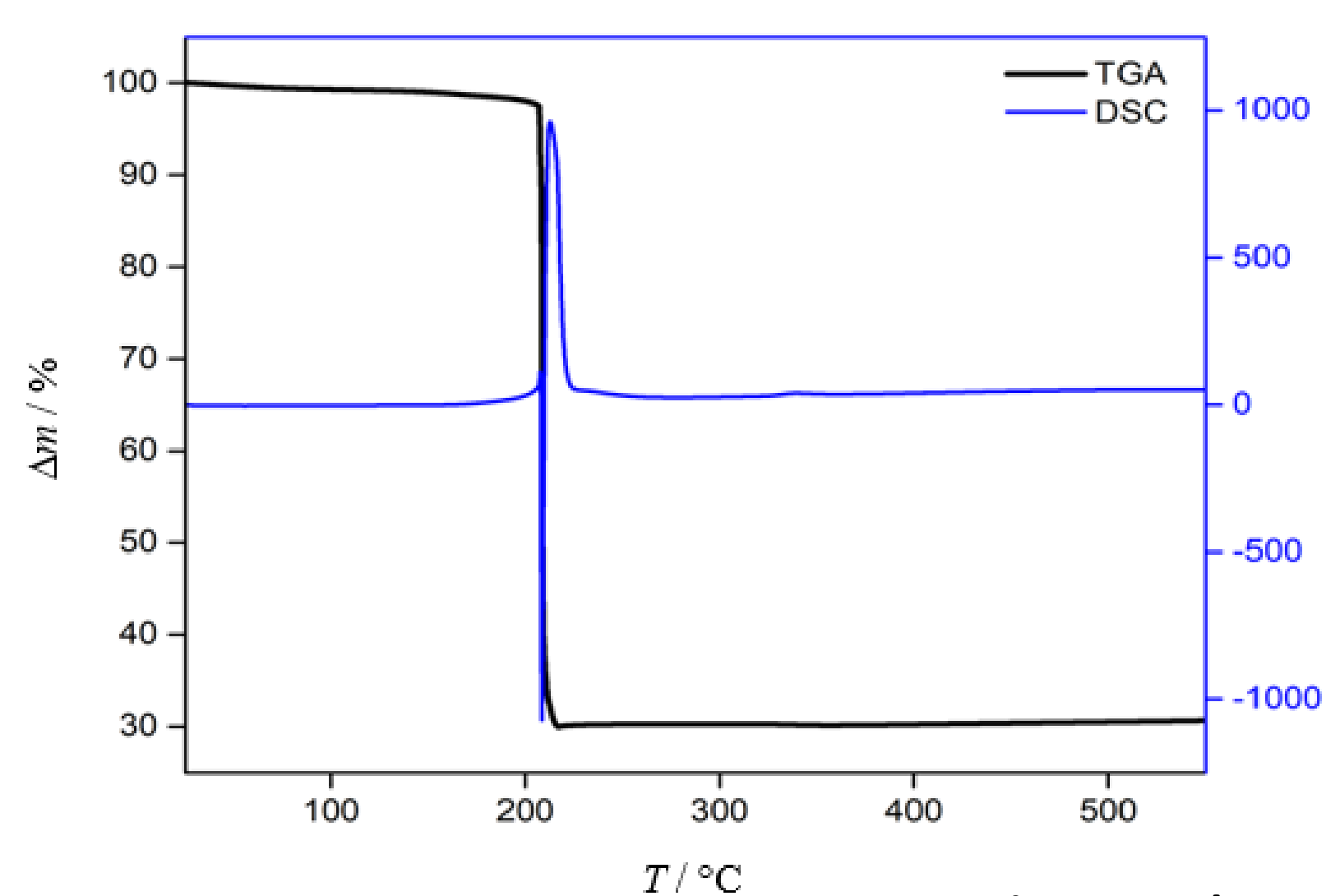


Figure 3. Thermal analysis K5 and K7

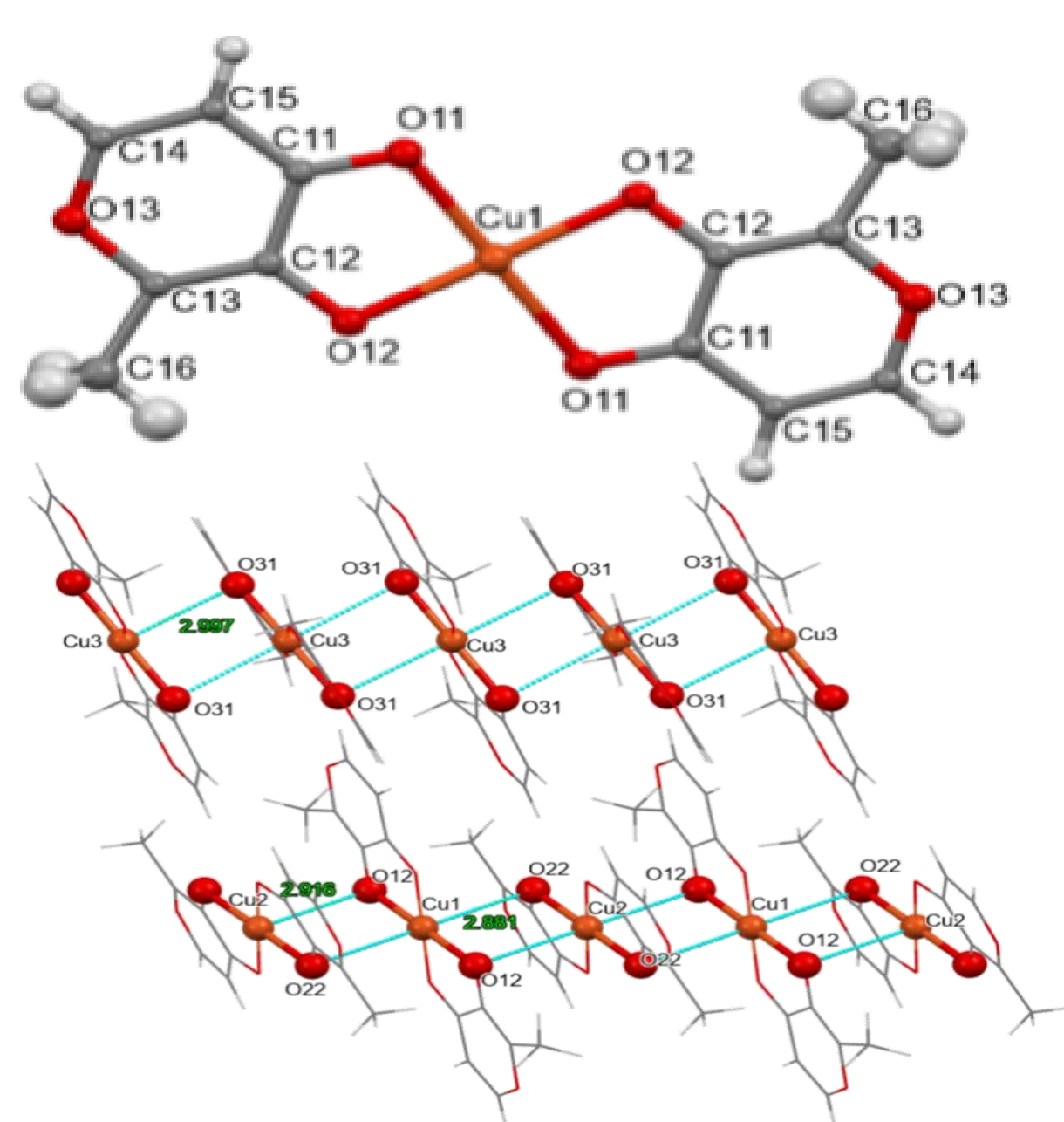


Figure 4. Single-crystal X-ray structure of complex K5: (a) molecular structure with atom-labeling scheme; (b) crystal packing showing intermolecular interactions.

Complex K5 is a mononuclear bis(maltolato)copper(II) complex with a 1:2 metal-to-ligand ratio. The four-coordinate Cu(II) center adopts an approximately square-planar geometry formed by four oxygen donor atoms from two deprotonated, bidentate *O,O*-donor ligands. The proposed structure is fully consistent with FT-IR, thermal, and elemental analyses, which confirm ligand deprotonation, stable chelate ring formation, and *O,O*-coordination around the metal center (Fig. 4.). The proposed structure is consistent with the FT-IR results, which confirmed ligand deprotonation and coordination through both oxygen donor sites, as well as with elemental and thermal analyses. Overall, the structural data support the formation of a stable bis(maltolato)copper(II) complex.

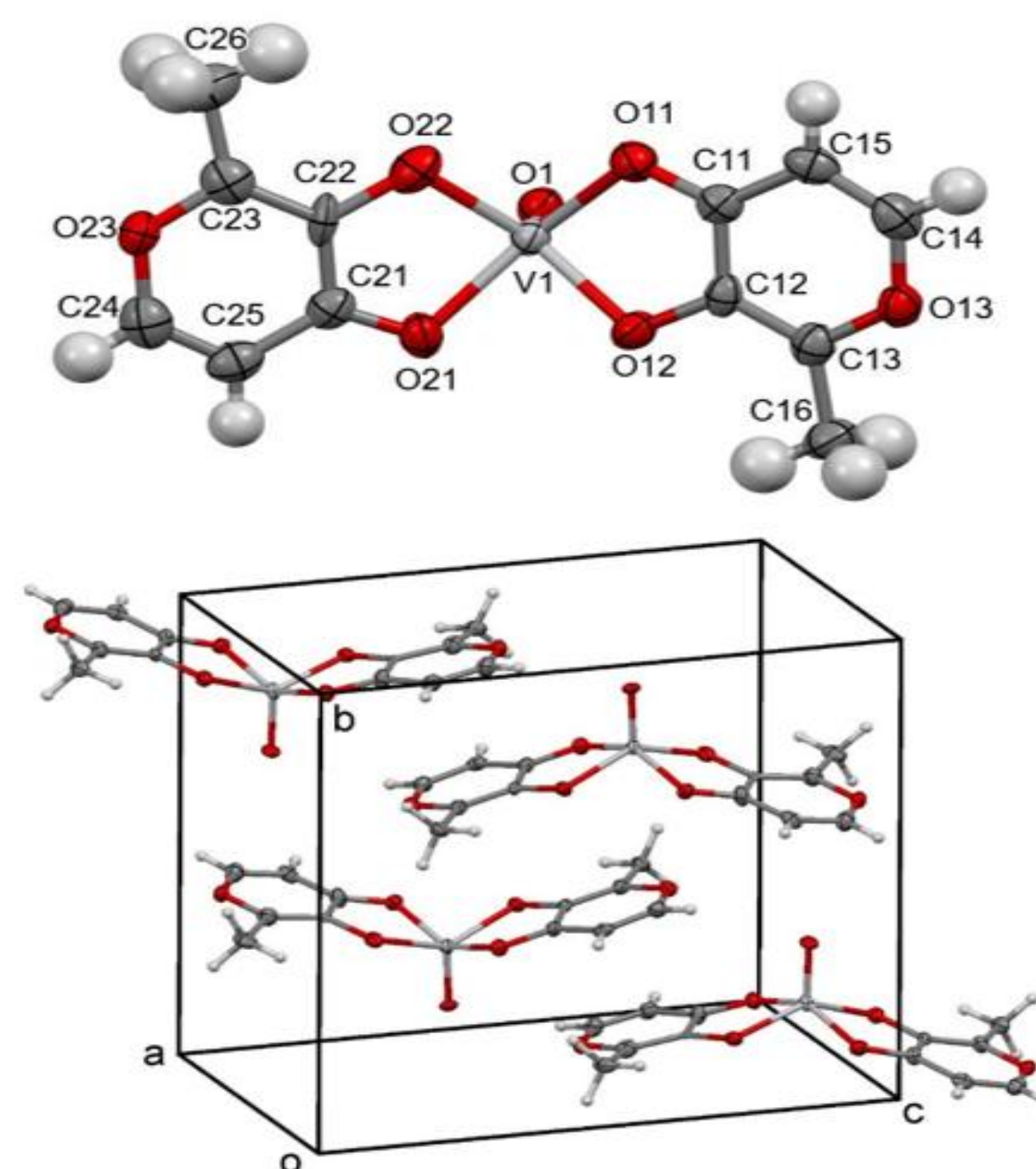


Figure 5. Single-crystal X-ray structure of complex K7: (a) molecular structure with atom-labeling scheme; (b) unit cell packing.

Complex K7 was confirmed by single-crystal X-ray diffraction as a mononuclear, solvent-free bis(maltolato)oxovanadium(IV) complex, VO(maltolato)₂ crystallizes in the monoclinic P2₁/n space group. The five coordinate V(IV) center adopts a square-pyramidal geometry with a 1:2 metal-to-ligand ratio. Two deprotonated maltolato ligands, each acting as a bidentate *O,O*-donors, occupying the equatorial plane with equivalent donor atoms in a *trans* arrangement, while a terminal oxo ligand (V=O) completes the coordination sphere of the metal center (Fig.5).

CONCLUSIONS

The synthesis and characterization of complexes K5 and K7 demonstrated the strong coordination ability of maltol toward transition metal ions. In both complexes, maltol acts as a bidentate *O,O*-donor ligand, coordinating through the carbonyl and deprotonated hydroxyl oxygen atoms. Complex K5 was identified as a mononuclear bis(maltolato)copper(II) complex with an approximately square-planar Cu(II) coordination environment, whereas K7 was confirmed as bis(maltolato)oxovanadium(IV), characterized by a square-pyramidal geometry with an axial V=O group. FT-IR spectroscopy supported ligand deprotonation and *O,O*-chelation, while thermal analyses revealed distinct decomposition profiles reflecting the different metal centers. K5 decomposed predominantly in a single step, whereas K7 showed a two-step degradation process, ultimately forming the corresponding metal oxide residues. These differences highlight the important influence of the metal center on the structural and thermal properties of the resulting coordination compounds. Overall, the complementary structural, spectroscopic, and thermal data confirmed the formation and stability of the investigated metal–maltol complexes.

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