



# Vibrational spectra and reinvestigation of the crystal structure of a polymeric copper(II)–orotate complex, $[\text{Cu}(\mu\text{-HOr})(\text{H}_2\text{O})_2]_n$ : The performance of new DFT methods, M06 and M05-2X, in theoretical studies

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## ABSTRACT

The crystal and molecular structure of a polymeric Cu(II)–orotate complex,  $[\text{Cu}(\mu\text{-HOr})(\text{H}_2\text{O})_2]_n$ , has been reinvestigated by single crystal X-ray diffraction. It is shown that several synergistic interactions: two axial Cu–O interactions; intramolecular and intermolecular hydrogen bonds; and  $\pi$ – $\pi$  stacking between the uracil rings contribute to the stability of the crystal structure. The Raman and FT-IR spectra of the title complex are reported for the first time. Comprehensive theoretical studies have been performed by using three unrestricted DFT methods: B3LYP; and the recently developed M06, and M05-2X density functionals. Clear-cut assignments of all the bands in the vibrational spectra have been made on the basis of the calculated potential energy distribution, PED. The very strong Raman band at  $1219\text{ cm}^{-1}$  is diagnostic for the N1-deprotonation of the uracil ring and formation of the copper–nitrogen bond, in this complex. The Cu–O (carboxylate) stretching vibration is observed at  $287\text{ cm}^{-1}$  in the IR spectrum, while the Cu–N (U ring) stretching vibration is assigned to the strong Raman band at  $263\text{ cm}^{-1}$ . The molecular structure and vibrational spectra (frequencies and intensities) calculated by the M06 functional method are very similar to the results obtained by the B3LYP method, but M06 performs better than B3LYP in calculations of the geometrical parameters and vibrational frequencies of the interligand O–H...O hydrogen bonding. Unfortunately, the M05-2X method seriously overestimates the strength of interligand hydrogen bond.

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## 1. Introduction

Orotic acid ( $\text{H}_3\text{Or}$ , 6-carboxyuracil, vitamin  $\text{B}_{13}$ ) has a pivotal role in the biosynthesis of nucleic acids in living organisms. It is the key precursor in the pathway to formation of all pyrimidine nucleotides [1]. It is also known to display bacteriostatic and cytostatic properties [2]. Recently, orotic acid and its complexes have attracted growing attention in medicine. Metal–orotates can penetrate the cell membranes, thus, they can be used in curing syndromes associated with a deficiency of calcium, magnesium, zinc, and iron [3–5]. The treatment with both vitamin  $\text{B}_{13}$  and Mg–orotate gives excellent results in prevention and treatment of heart diseases [6]. It should be emphasized that copper–orotates are used as ingredients in pharmaceutical compositions for curing neoplastic disease [7] and compositions for treating skin, hair and nails [8].

In the last 10 years many research groups performed extensive studies on application of orotic acid as a polydentate ligand in coordination chemistry [9–23].

The multifunctionality of the orotate anions offers interesting possibilities for supramolecular assemblies in crystal engineering. Metal ion coordination may occur through the two carboxylate O atoms as well as the two N atoms of the pyrimidine ring and two carbonyl oxygen atoms. Recently, our single crystal X-ray diffraction study on *cis*- $[\text{Cu}(\text{HOr})(\text{NH}_3)_2]$  has revealed the additional, unusual coordination site of the orotate ligand ( $\text{HOr}^{2-}$ ), namely, the  $\pi(\text{C}=\text{C})$  bond of the uracilate ring [13]. Soylu et al. [21] also reported a similar Cu– $\pi$  interaction in the dimeric complex,  $[\text{Cu}_2(\text{HOr})_2(\text{H}_2\text{O})_4]$ . Theoretical studies have shown that the dispersion energy plays a significant role in this noncovalent Cu– $\pi$  binding force [14].

A reliable assignment of the vibrational spectra of metal–orotates is crucial for the further spectroscopic studies on interactions with other molecules in the biological environment or in the supramolecular assemblies. In a series of papers we reported detailed experimental and theoretical studies of the vibrational spectra and molecular structures of *cis*- $[\text{Ni}(\text{HOr})(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}$  [11], *cis*- $[\text{Pt}(\text{HOr})(\text{NH}_3)_2]$  [12], *cis*- $[\text{Cu}(\text{HOr})(\text{NH}_3)_2]$  [13,14], and  $[\text{Ni}(\text{HOr})(\text{NH}_3)_2(\text{H}_2\text{O})_2]$  [15].

In an attempt to make a new Cu(II)–orotate complex, we synthesized blue crystals and performed the single crystal X-ray

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diffraction study. The results have shown a polymeric structure,  $[\text{Cu}(\mu\text{-HOR})(\text{H}_2\text{O})_2]_n$ . This compound was obtained earlier (by a different method), but its structure was reported only in the form of a short communication [9]. Nevertheless, our X-ray analysis has revealed new interesting details in the crystal structure of this complex and intermolecular hydrogen bonds (which are missing in Ref. [9]).

One of the goals of this work is to make a clear-cut assignment of the experimental vibrational spectra of this complex on the basis of the calculated potential energy distribution, PED. This is important because of some discrepancies in the literature regarding the vibrational assignment of the IR spectra of metal orotates, for example, the Cu–O and Cu–N stretching vibrations have been reported at about 600 and 450  $\text{cm}^{-1}$ , respectively [20,21]. This assignment is not supported by our previous experimental and theoretical study [14].

The FT-IR and Raman spectra of the title complex are reported for the first time. The theoretical studies have been performed by means of three unrestricted DFT methods: B3LYP and the newly developed M05-2X and M06 functionals. The latter method was recommended for application in organometallic and inorganometallic chemistry [24]. Therefore, in this work, we have assessed the performance of the M05-2X and M06 methods for their ability to predict the molecular structure, hydrogen bonding and the vibrational frequencies of the copper(II)–orotate complex.

## 2. Experimental

### 2.1. Preparation

The aqueous solutions of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (5 mmol, 25  $\text{cm}^3$ ) and  $\text{NaHCO}_3$  (5 mmol, 25  $\text{cm}^3$ ) were added to a suspension of orotic acid (5 mmol) in water (25  $\text{cm}^3$ ). The reaction mixture was stirred and heated at 353 K for 1 h in a temperature-controlled bath. A small amount of a precipitate (containing an unreacted ligand) was separated by filtration, while the clear filtrate was allowed to evaporate to about a half of the volume. After a few days blue crystals were formed. They were filtered off, washed with 10  $\text{cm}^3$  of cold water and dried in a desiccator. The results of elemental analysis have shown that the complex has the formula  $[\text{Cu}(\mu\text{-HOR})(\text{H}_2\text{O})_2]_n$ . Found: C, 23.66%; H, 2.31%; N, 11.11%. Calcd.: C, 23.68%; H, 2.38%; N, 11.04%. It should be emphasized that this procedure differs from that reported in Ref. [9] (where the title complex was obtained by a demethylation of orotic acid ester).

### 2.2. X-ray analysis

The X-ray diffraction data were collected using an Oxford Diffraction X'Calibur four-circle automatic single crystal diffractometer with CCD area detectors (graphite monochromator, Mo  $K\alpha$  radiation). The intensity data were corrected for Lorentz, absorption and polarization effects. The structure was solved by direct methods using the SHELXS-97 program [25] and refined by the full-matrix least-squares method based on  $F^2$  using SHELXL-97 [26]. Non-hydrogen atoms were refined with anisotropic thermal parameters, hydrogen atoms were included from the difference Fourier  $\Delta\rho$  maps and refined with isotropic thermal parameters. Molecular drawings were obtained using DIAMOND [27].

### 2.3. Raman and infrared spectral measurements

The Raman spectrum of the title complex was recorded on an Horiba Jobin Yvon dispersive Raman Spectrometer HR800 equipped with a microscope and Ar–Kr lasers, using an Ar 514.5 nm laser line, with a resolution of 2.5  $\text{cm}^{-1}$ . The spectrum was measured in Sol-Gel Nanotechnology Materials Laboratory of Lower

Silesian Centre for Advanced Technologies in Wrocław. The FT-IR spectrum in the region 4000–400  $\text{cm}^{-1}$  was measured on Bruker IFS 113V spectrometer (with a resolution of 2  $\text{cm}^{-1}$ ) using KBr pellets. The far-infrared spectrum (600–50  $\text{cm}^{-1}$ ) was recorded on FT-IR Bruker IFS 66/S spectrometer (with a resolution of 2  $\text{cm}^{-1}$ ) using Nujol mull technique and polyethylene windows.

### 2.4. Theoretical

The investigated compound is an open-shell system ( $d^9$  electron configuration of Cu(II) cation). This requires the use of the unrestricted DFT methods for calculations of an electronic structure. Calculations were performed for two models: an isolated  $[\text{Cu}(\text{HOR})(\text{H}_2\text{O})_2]$  complex and the supramolecular system  $[\text{Cu}(\text{HOR})(\text{H}_2\text{O})_2] \cdot \text{CH}_2\text{O}$ , containing formaldehyde above the copper complex (the latter model was used to simulate formation of the Cu–O axial bond). The optimized geometry, harmonic frequencies, IR intensities and Raman scattering activities were computed using the density functional gradient corrected three-parameter hybrid functional UB3LYP [28,29], and two newly developed DFT hybrid methods UM05-2X [30,31] and UM06 [24]. All calculations were based on an unrestricted mechanism, however, U will be omitted from these abbreviations, in the remaining text. The calculated ground electronic state for the title complex is doublet,  $^2A'$ .

It has been shown in our earlier studies [14,15] that a reliable prediction of both the molecular structure and vibrational spectra of transition metal complexes can be obtained using combined basis sets: the polarized valence double- $\xi$  basis set, D95V(d,p) [32], for all atoms of the ligands, in conjunction with the LanL2DZ effective core potential and valence basis set [33] for metal atoms. The use of a larger basis set (aug-cc-pVTZ) for all atoms does not improve the results, and is computationally very expensive [14]. Thus, all calculations in this work have been performed with the combined D95V(d,p) and LanL2DZ basis sets.

The calculated Raman scattering activity coefficients,  $S_i^R$ , were converted to relative Raman intensities using the following relationship [34]:

$$I_i^R = C \cdot (\nu_0 - \nu_i)^4 \cdot \nu_i^{-1} \cdot B_i^{-1} \cdot S_i^R \quad (1)$$

where  $\nu_0$  is the frequency of the laser excitation line (19,436.3  $\text{cm}^{-1}$ , in this study),  $\nu_i$  is the frequency of normal mode ( $\text{cm}^{-1}$ ),  $C$  is a normalization factor ( $10^{-14}$ ) and  $B_i$  is a temperature factor which accounts for the intensity contribution of excited vibrational states, and is represented by the Boltzmann distribution:

$$B_i = 1 - \exp\left(-\frac{h \cdot \nu_i \cdot c}{k \cdot T}\right) \quad (2)$$

In Eq. (2),  $h$ ,  $k$ ,  $c$ , and  $T$  are Planck and Boltzmann constants, speed of light and temperature in Kelvin, respectively.

To allow the comparison of the corresponding vibrational frequencies calculated by different methods, normal coordinate analysis was carried out at each level of theory. A non-redundant set of 54 symmetrized internal coordinates for 20 atoms of  $[\text{Cu}(\text{HOR})(\text{H}_2\text{O})_2]$  was defined, as recommended by Pulay et al. [35]. The internal coordinates were analogous to those reported in our earlier studies on similar compounds [15,36]. The procedure for normal coordinate analysis was described previously [36]. The detailed vibrational assignment of the experimental spectra has been made on the basis of the calculated potential energy distributions (PEDs) [37]. All DFT computations have been performed with the Gaussian 03 (Rev. E.01) set of programs [38].

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