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# Structure and Vibrational Spectra of 1:1 Chloranilic Acid (CLA)—Tetramethylpyrazine (TMP) Complex

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In searching for new molecular materials the crystals of 1:1 complexes of tetramethylpyrazine (TMP) with chloranilic acid (CLA) were grown. In the crystalline lattice of TMP.CLA infinite chains of hydrogen bonded components are formed. Very strong ($d_{(O\cdots N)} = 2.692(2)$ Å) hydrogen bonds without proton transfer are present. The components of the complex form stacks of parallel arrangement with the distance typical of van der Waals interaction. One can conclude that in packing, interactions via hydrogen bonds play a decisive role. In the IR spectrum one observes a broad, continuous absorption with well resolved trio typical of strong hydrogen bonds. A detailed analysis of IR and Raman spectra in the low frequency region related to deformation vibrations of $CH_3$ groups shows that strong interaction via hydrogen bonding only slightly affects the dynamics of these groups.

**KEY WORDS:** Chloranilic acid-tetramethylpyrazine complex; structure; IR; Raman spectra.

## INTRODUCTION

Quite recently it has been shown that chloranilic acid (CLA) can form a variety of molecular complexes that seems to be interesting from the point of view of supramolecular chemistry [1–7]. The CLA molecule exhibits on one hand the electron-acceptor properties and on the other hand acidic properties leading to formation of hydrogen bonds. In the case of stronger bases the proton-transfer H-bonded ion pairs can be formed. Benzoquinones, to which CLA belongs, are interesting from the point of view of electron transfer reactions in biological systems as well [8–10]. But complexes with nitrogen bases seem to be most attractive. Ishida and Kashino reported the formation of ionic crystals composed of CLA and pyridine and 1,2-diazine [1] of composition 1:1 and

1:2, as well as with pyrazole and imidazole [3] having interesting supramolecular architecture. In the case of pyrimidine and pyrazine [2] as N-acceptors, the 1:2 complexes with bifurcated H-bondings are formed: i.e. both OH groups simultaneously form H-bonds with N-bases and intramolecular ones with carbonyl groups. Also of interest are the structures of complexes obtained by Zaman *et al.* [5–7] with derivatives of bipyridils forming the complex supramolecular architectures. CLA as pointed out can be treated as a component of supramolecular synthons in crystal engineering. Finally one can mention some new aspects of chemistry of metal complex compounds [11, 12] with participation of CLA, and some analytical and electrochemical applications of CLA [13–14].

Because we undertook in our studies the problem of dynamics of methyl groups in molecular complexes (both H-bonded and charge transfer (CT)), it seemed justified to carry out the structural study on the CLA complex with tetramethylpyrazine (TMP). In this case a stable complex of 1:1 composition is formed. The aim of the present paper was the X-ray study as well as IR and Raman spectra tending towards the recognition of the influence of complexation on the dynamics of $CH_3$ groups.

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**Table I.** Crystal Data and Structure Refinement for 1:1 Chloranilic Acid–Tetramethylpyrazine Complex

| | |
|---|---|
| Identification code | CLA.TMP |
| Empirical formula | $C_{14}H_{14}Cl_2N_2O_4$ |
| Formula weight | 345.17 |
| Temperature (K) | 100 (2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| Unit cell dimensions | |
| $a$ (Å) | 12.327(2) |
| $b$ (Å) | 4.699(1) |
| $c$ (Å) | 13.454(3) |
| $\beta$ (°) | 105.06(3) |
| Volume (Å$^3$) | 752.6(3) |
| $Z$ | 2 |
| Calculated density (Mg/m$^3$) | 1.523 |
| Absorption coefficient (mm$^{-1}$) | 0.450 |
| $F(0\,0\,0)$ | 356 |
| Crystal size (mm) | $0.30 \times 0.25 \times 0.20$ |
| $\Theta$ range for data collection (°) | 3.94–28.43 |
| Index ranges | $-16 \leq h \leq 16$ |
| | $-3 \leq k \leq 6$ |
| | $-17 \leq l \leq 17$ |
| Reflections collected/unique | 4556/1746 ($R_{int} = 0.0367$) |
| Absorption correction | Empirical (SHELXA) |
| Max. and min. transmission | 0.9153 and 0.6767 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data [$I > 2\sigma(I)$]/ parameters | 1370/128 |
| Goodness-of-fit on $F^2$ | 0.998 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.034$, $wR_2 = 0.092$ |
| $R$ indices (all data) | $R_1 = 0.045$, $wR_2 = 0.109$ |
| Largest diff. peak and hole (eÅ$^{-3}$) | 0.346 and $-0.370$. |

## EXPERIMENTAL

The dark-pink crystals of the 1:1 CLA.TMP complex were grown from acetone.

The X-ray diffraction studies were performed on a Kuma KM4CCD $\kappa$-axis four circle diffractometer equipped with an Oxford Cryosystem Cooler using graphite monochromated MoK$_\alpha$ radiation. The data were corrected for Lorentz and polarization effects, as well as for absorption. The empirical method using the SHELXA program from the SHELXL-97 package was applied.

The structure was solved by direct methods with SHELXS-97 [15] and refined by the full-matrix least-squares methods using the SHELXL-97 [16] program. Non-hydrogen atoms were refined with anisotropic thermal parameters. All the H atoms were found from different synthesis and refined with isotropic thermal parameters. The crystal data and structure refinements are summarized in Table I.

The infrared spectra were recorded in Nujol suspensions (KBr or CsI windows) using a FTIR Bruker IFS 113 V spectrophotometer. The Raman spectra of powder samples were recorded on a Nicolet Magma 860 FT Raman spectrometer. A diode-pumped Nd: YAG laser was the excitation source, with a power of ca. 200 mW. Backscattering geometry was applied. The resolution was set up for $2\,cm^{-1}$; 512 scans were measured. The separation of the broad absorption was performed by using the GRAMS program [17]. The three components were fitted to the Gaussian profiles.

## RESULTS AND DISCUSSION

### The Crystal and Molecular Structure

The main element of the crystal structure of CLA.TMP complex are infinite hydrogen bonded chains along the $a$-axis shown in Fig. 1. The bond lengths and angles of CLA and TMP components are listed in Table II. The details relating to the atomic coordinates with isotropic displacement parameters for H-atoms and anisotropic displacement parameters for non-H-atoms and all crystallographic data are deposited at the Cambridge Crystallographic Data Center (CCDC No 249433).

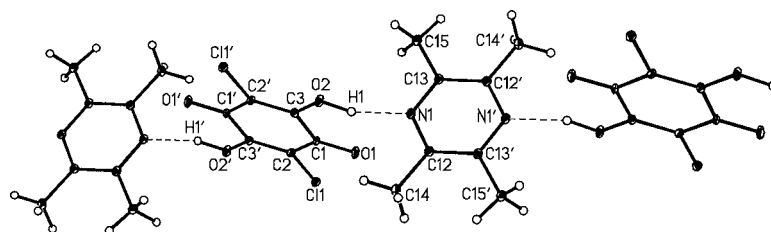The core rings of CLA and TMP molecules forming infinite chains are almost ideally planar (rms values are



**Fig. 1.** Infinite chain of H-bonded CLA.TMP molecules. Atoms marked with a prime (′) are at the symmetry position $(-x + 1, -y + 1, -z + 1)$ for CLA and $(-x, -y + 1, -z + 1)$ for TMP, respectively.

**Table II.** Selected Bond Lengths [Å] and Angles [°] for CLA.TMP

| CLA molecule | |
|---|---|
| C(1)—C(2) | 1.723(2) |
| O(1)—C(1) | 1.227(2) |
| O(2)—C(3) | 1.324(2) |
| C(2)—H(1) | 0.93(3) |
| C(2)—C(3′) | 1.350(3) |
| C(2)—C(1) | 1.456(3) |
| C(3)—C(1) | 1.503(3) |
| TMP molecule | |
| N(1)—C(13) | 1.344(3) |
| N(1)—C(12) | 1.349(3) |
| C(15)—C(13) | 1.507(3) |
| C(15)—H(5) | 0.95(5) |
| C(15)—H(6) | 0.92(5) |
| C(15)—H(7) | 0.81(5) |
| C(12)—C(13′) | 1.399(3) |
| C(12)—C(14) | 1.497(3) |
| C(14)—H(2) | 0.90(3) |
| C(14)—H(3) | 0.95(3) |
| C(14)—H(4) | 1.02(4) |
| CLA molecule | |
| C(3)—O(2)—H(1) | 121(1) |
| C(3′)—C(2)—C(1) | 120.7(2) |
| C(3′)—C(2)—Cl(1) | 121.2(2) |
| C(1)—C(2)—Cl(1) | 118.1(1) |
| O(2)—C(3)—C(2′) | 121.7(2) |
| O(2) C(3)—C(1) | 117.3(2) |
| C(2′)—C(3)—C(1) | 121.0(2) |
| O(1)—C(1)—C(2) | 123.2(2) |
| O(1)—C(1)—C(3) | 118.5(2) |
| C(2)—C(1)—C(3) | 118.3(2) |
| TMP molecule | |
| C(13)—N(1)—C(12) | 119.7(2) |
| N(1)—C(12)—C(14) | 117.4(2) |
| C(13′)—C(12)—C(14) | 122.7(2) |
| N(1)—C(13)—C(12′) | 120.4(2) |
| N(1)—C(13)—C(15) | 117.3(2) |
| C(12′)—C(13)—C(15) | 122.3(2) |

*Note.* Symmetry code: (′) $-x + 1, -y + 1, -z + 1$ for CLA and $-x, -y + 1, -z + 1$ for TMP.

equal to 0.0059 for CLA and 0.0022 for TMP). These rings are oriented one to each other by 84.4(1)° (see Fig. 2). Both CLA and TMP molecules are stacked along the *b*-axis as shown in Fig. 3. Between these stacks there are contacts formed by methyl groups of TMP and oxygen and chlorine atoms of CLA (see Table III). The geometry of O—H· · ·N hydrogen bonds is as follows:

R(OH) = 0.93(3) Å, R(H· · ·N) = 1.79(3) Å, R(O· · ·N) = 2.692(2) Å and < OHN = 161(3)°. These data show that we are dealing with rather strong hydrogen bonds. Comparing the bond lengths and angles of CLA and TMP in the complex with those of free components reported in [18, 19] one can formulate the following remarks. There are no detectable differences in the geom-
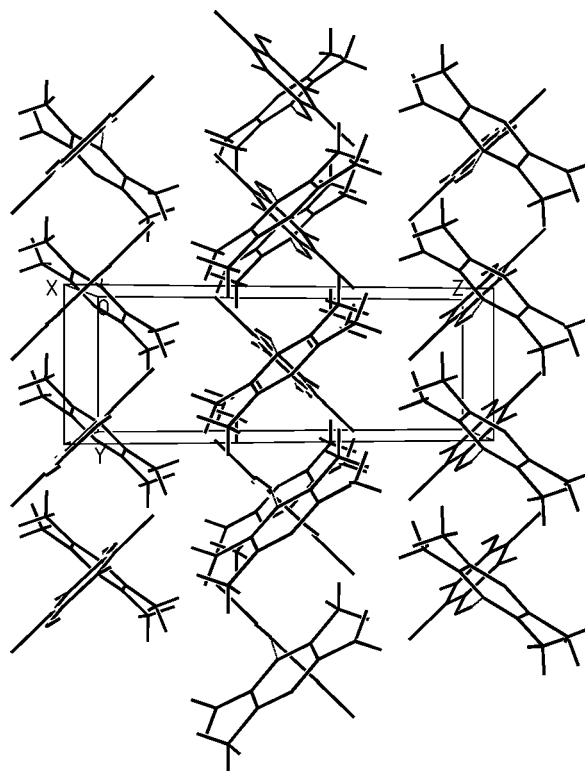


**Fig. 2.** Arrangement of molecules seen along the *a*-axis.

etry after complexation except the geometry of hydrogen bridges. In the case of CLA molecule itself there is an intramolecular highly bent OH· · ·O bridge, while in the TMP.CLA complex this bridge is practically broken. The
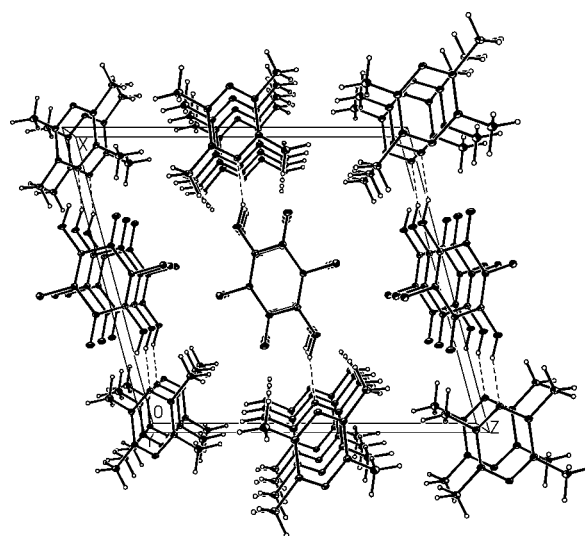


**Fig. 3.** Stacking of CLA and TMP molecules along the *b*-axis.

**Table III.** Hydrogen Bonds and Short Contacts

| D···A | D···A (Å) | D—H (Å) | H···A (Å) | <(DHA) (°) |
|-------|-----------|---------|-----------|-------------|
| O(2)—H(1)···N(1) | 2.692(2) | 0.93(3) | 1.79(3) | 161(3) |
| O(2)—H(1)···O(1) | 2.697(2) | 0.93(3) | 2.39(3) | 99(2) |
| C(14)—H(4)···O1)i | 3.292(3) | 1.02(4) | 2.47(4) | 137(3) |
| C(14)—H(4)···O(2) | 3.599(3) | 1.02(4) | 2.81(4) | 135(3) |
| C(15)—H(6)···O(2)ii | 3.520(3) | 0.95(5) | 2.70(4) | 145(3) |
| C(15)—H(7)···O(1)iii | 3.388(3) | 0.81(5) | 2.92(5) | 118(4) |
| C(15)—H(7)···Cl(1)iii | 3.732(3) | 0.81(5) | 3.07(5) | 140(4) |

*Note.* Symmetry code: (i) $x, y + 1, z$; (ii) $x, y - 1, z$; (iii) $x, -y + 1/2, z + 1/2$.

new O—H···N bridge is markedly stronger. Although the O···O intramolecular distance (2.697(2) Å) is comparable with the O···N intermolecular one, the linearity in the latter case is much better. Moreover, the van der Waals radius of N is about 0.05 Å longer than that of O. Note that the intermolecular OH···O hydrogen bond formed in the pure CLA is much longer at 2.769(1) Å. As will be shown, the geometry of OH···N hydrogen bond in CLA.TMP complex finds the reflection in the IR spectrum.

**IR and Raman Spectra**

In the IR spectrum, as shown in Fig. 4, it is observed that there are very well resolved Hadzi's trio [20] with maxima at ca 1100, 1900 and 2750 cm$^{-1}$ with an extra band at 2400 cm$^{-1}$. Its origin is usually ascribed to the Fermi resonance between the stretching $\nu$(OH) vibrations and 2$\delta$(OH) and 2$\gamma$(OH) overtones of deformation vibrations. However the positions of overtones fit neither to maxima nor to minima of broad absorption.

Qualitatively, the observed picture fits to that generated by assuming the asymmetric double minimum potential for the proton motion expressed by a 4th order polynomial [21]

$$V(r, R) = a_2(R)r^2 + a_3(R)r^3 + a_4(R)r^4$$

where $r$ is the coordinate of the protonic stretching vibrations, $R$-the coordinate of bridge vibrations while $a_2$, $a_3$ and $a_4$ are parameters depending on $R$. The profiles of the
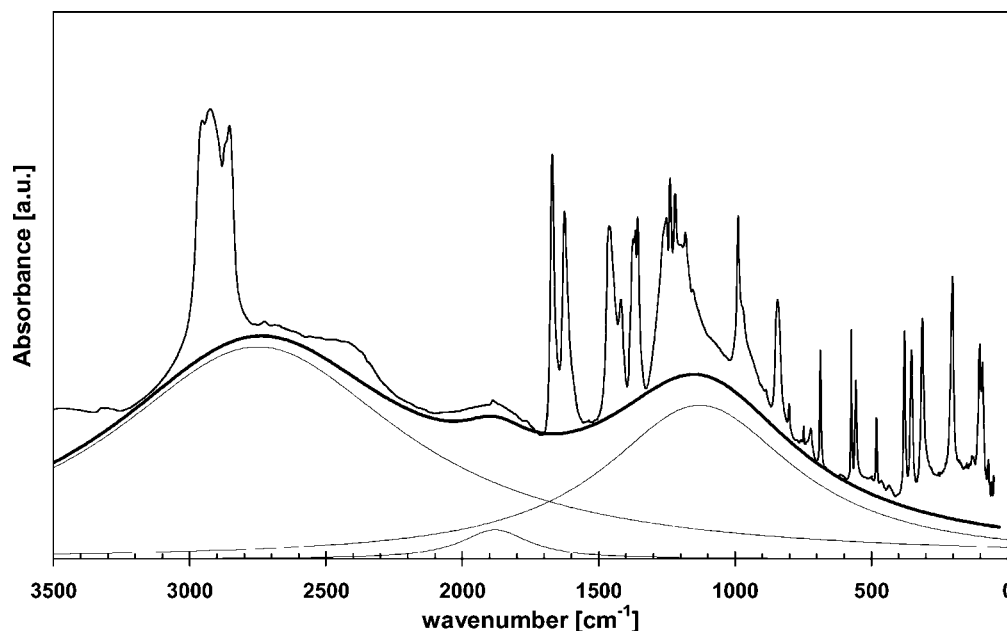


**Fig. 4.** IR spectrum of CLA.TMP complex with separation of broad $\nu$(OH···N) band consisting of three sub-bands centred at 2750, 1900 and 1150 cm$^{-1}$.
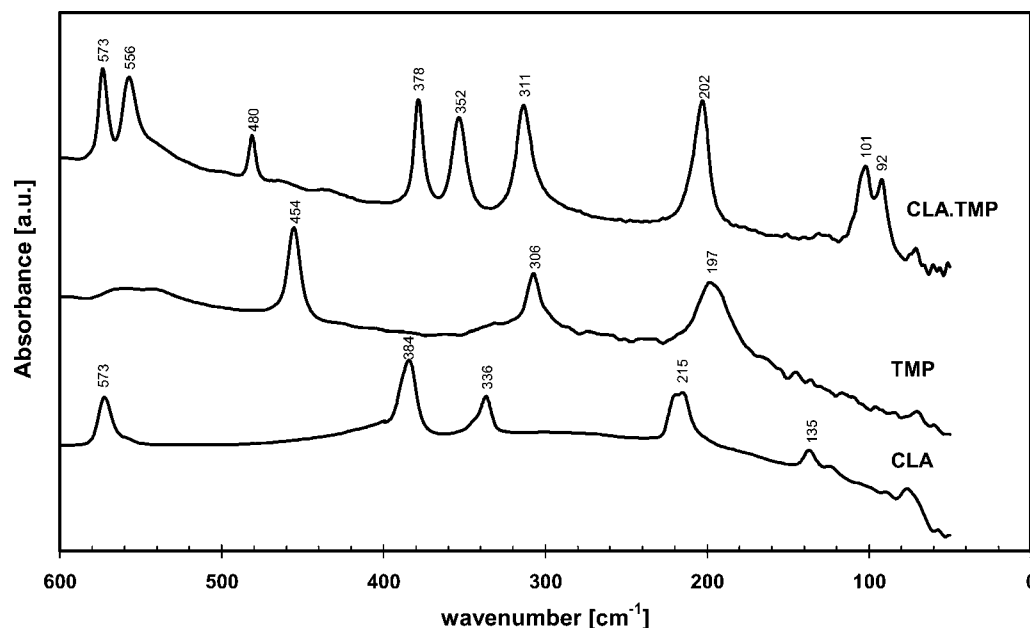
**Fig. 5.** IR spectra in the low frequency region of CLA, TMP, and their 1:1 H-bonded complex –CLA.TMP.

trio absorption components result from the coupling of anharmonic stretching protonic vibrations with the bridge vibrations, which are overdamped due to the interaction with the lattice phonons; one can apply a stochastic model [22, 23], i.e. we are dealing with a quasistatic distribution of the bridge length. The absorption picture observed for CLA.TMP is very close to that obtained from calculations for asymmetric O—H···O hydrogen bonds of 2.60 Å length [24]. This corresponds to the O—H···N length of about 2.65 Å which is close to that of the CLA.TMP complex in the solid state.

Therefore our interpretation of the IR spectrum of CLA.TMP complex would be that the band at $1100\,\mathrm{cm}^{-1}$ corresponds to the $0 \to 1$ transition, the band at $1900\,\mathrm{cm}^{-1}$ to $1 \to 2$ and $2750\,\mathrm{cm}^{-1}$ to $0 \to 2$. From the calculations it follows [25] that integrated intensities of $0 \to 1$ and $0 \to 2$ bands should be similar while the $1 \to 2$ band should be very weak, and this is in agreement with observation.

One cannot exclude, that the complex shape of broad absorption is due to both the splitting of vibrational levels resulting from the asymmetric double minimum potential and the Fermi resonance. An alternative to the above interpretation would be a scheme assuming that the high frequency wing of the broad absorption consists of two components: one of them close to $3000\,\mathrm{cm}^{-1}$ which fits better to the $0 \to 2$ transition and the second one close to $2400\,\mathrm{cm}^{-1}$ arising from the Fermi resonance.

The main task of this work, in addition to the X-ray diffraction studies, was to acquire some information about the influence of complexation on the dynamics of methyl groups which is best reflected in modes located below $600\,\mathrm{cm}^{-1}$. In order to assign the bands in the IR and Raman spectra of the CLA.TMP complex in this frequency region, we compared the spectra measured separately for TMP, CLA, and their complex. Figs. 5 and 6 present the IR and Raman spectra for these three compounds. Analysis of the spectra was performed based on DFT calculations by using the GAUSSIAN program [26].

The comparison of spectra presented in Figs. 5 and 6 shows conclusively that we are dealing with the summing of spectra ascribed to separate components. There are observed only negligible changes in frequencies and relative intensities. A meaningful change can be noticed only for three modes observed in the IR spectra. Thus the mode at $454\,\mathrm{cm}^{-1}$ assigned to C—CH$_3$ wag vibration is shifted on complexation to $480\,\mathrm{cm}^{-1}$, while that at $306\,\mathrm{cm}^{-1}$ (C—CH$_3$ bend) shifts to $311\,\mathrm{cm}^{-1}$ and that at 197 (CH$_3$ tors.) goes to $202\,\mathrm{cm}^{-1}$. The bands at 524, 476, 381 and $281\,\mathrm{cm}^{-1}$ in the Raman spectra of the CLA.TMP complex correspond to the bands observed in the spectrum of TMP, in which the main contribution comes from the deformation vibrations of the CH$_3$ groups coupled to varying degrees with the ring vibrations. Thus, their positions in the Raman spectrum for the CLA.TMP complex are almost unchanged.
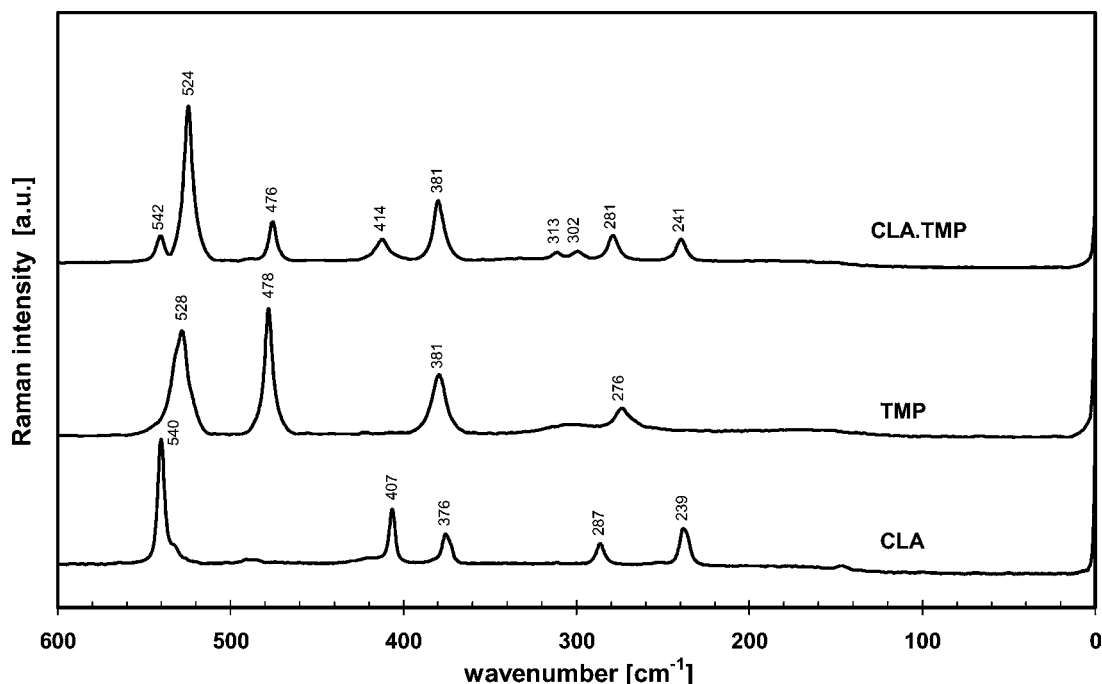
**Fig. 6.** Raman spectra in the low frequency region of CLA, TMP, and their 1:1 H-bonded complex—CLA.TMP.

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