Structure and tunneling splitting spectra of methyl groups of tetramethylpyrazine in complexes with chloranilic and bromanilic acids.

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Streszczenie

The crystal and molecular structure of the 2,3,5,6-tetramethylpyrazine (TMP) complex with 2,5-dibromo-3,6-dihydroxy-p-quinone (bromanilic acid, BRA) has been studied and the results are compared with TMP CLA (2,5-dichloro-3,6-dihydroxy-p-quinone (chloranilic acid, CLA) complex. The X-ray structure of TMP BRA complex indicates the formation of dimeric units, in which two BRA^- anions are connected by two O–H···O (2.646(2) Å) hydrogen bonds, whereas the cations and anions are joined together by strong N^+–H···O^- (2.657(2) Å) hydrogen bonds. The results are analyzed in terms of both the methyl group surroundings and the C–H···O and N^+–H···O^- (or N···H–O) bridge formations. Both effects, the strength of the N^+–H···O^- hydrogen bonds and steric hindrance for the rotations, are responsible for the CH_3 group dynamics. For the TMP CLA and TMP BRA complexes, the inelastic neutron backscattering spectra were also investigated. In the case of TMP CLA, four tunneling signals have been observed in the energy range ±30 μeV, which indicates four inequivalent methyl groups in the crystal structure at the lowest temperature. No tunneling splitting is observed in the case of the TMP BRA complex, most probably due to the overlapping with the elastic peak. The tunneling results are consistent with the ^1H NMR spin–lattice relaxation time investigations in a wide temperature range, which also point to the CH_3 group tunneling effect in the case of TMP CLA.

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