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Review

H-bonded complexes between pyrazines containing methyl groups and strong proton donors: structure and dynamics

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ABSTRACT

Pyrazine belongs to an interesting class of heterocyclic compounds of moderate basicity that are capable of forming various molecular complexes of intriguing architecture, particularly from the crystallo-chemical point of view. The presence of methyl (-CH_3) groups in the pyrazine molecule is of interest to researchers because of the effect of the charge transfer phenomenon on the rotational barrier of the -CH_3 group. In the present review we analyzed the structures of various molecular complexes containing proton donors such as *p*-nitrophenol, picric acid, squaric acid, triiodo hydride, nitric acid and, in particular, chloranilic and bromanilic acids. The interactions, mainly via hydrogen bonds, lead to a variety of crystal structures mostly due to proton transfer to the nitrogen atoms in pyrazine. In this review, the structures of complexes and their crystal-lattice packing studied using X-ray diffraction are discussed. The variety of hydrogen bonds in the complexes studied is best reflected in their infrared absorption spectra. In many cases the absorption continua typical of the strong hydrogen bonds are present. Inelastic neutron scattering (INS) spectra were used to analyze dynamics. The results of tunneling splitting ascribed to methyl groups were also found interesting. This aspect is given focus in this work. One of the main observations from these studies was that methyl groups in the solid state of the molecular complexes rotated more freely than those in pure methyl derivatives of pyrazine.

KEYWORDS: molecular complexes, pyrazine, organic acid, proton donor, proton acceptor, methyl group dynamics, infrared, inelastic neutron scattering, hydrogen bond, proton transfer

INTRODUCTION

In this review we present an overview of the current literature reporting on complexes between methyl derivatives of pyrazine and strong proton donors, in the light of our review article published in Polish [1]. This article consists of two parts. The ability of proton donors to form interesting self-associated and hydrogen-bonded complexes is discussed in the first part. The second part deals with the capabilities of proton acceptors (electron donors), represented by pyrazine and its methyl derivatives, to form complexes.

In the latter part we also discuss representative examples including the following compounds: cyclometalated iridium(III) complexes showing highly efficient phosphorescence [2], coordination polymers formed by 2-methylpyrazine with copper(II) [3], a pyrazine-bridged pentanuclear copper(II) complex [4], and the silver(I) sulfonate complexes with pyrazine derivatives [5-7]. The report devoted to the complex of tetramethylpyrazine (TMP) with *p*-nitrophenol is particularly interesting from our personal point of view [8].

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Other papers related to the pyrazine derivatives report on the following topics: carbonyl-pyrazine complexes with transition metals [9], magnetic studies of copper(II) and copper(I) complexes of methylpyrazines [10], and structural, thermal and electrical studies on the selected transition metal compounds of 2-methylpyrazine [11].

Several important results on the charge transfer effect have been obtained from the thermal- and light-induced electron transfer between iron(II) and cobalt(III) mediated by bridging pyrazine ligands [12]. Also important are the results of studies on the copper(II) complex with 2,5-dimethylpyrazine, in particular theoretical calculations of magnetic dimensionality and magnetic exchange interactions [13]. Worth mentioning are the papers of Shi *et al.*, which are devoted to the synthesis, structure and magnetism of one- and three-dimensional cobalt(II) complexes of 2,5-dimethylpyrazine-1,4-dioxide [14, 15, 16]. Novel copper(I) 2,3-dimethylpyrazine coordination compounds have been reported as well [17]. The formation of complexes between pyrazine-N,N'-dioxide and tetracyanoethylene with electron donor-acceptor (EDA) bonding has also been observed [18]. The protonation of coordinated 2-methylpyrazine and 4,4'-bipyridine as a probe of π-donor potential of ruthenium(II) has also been reported [19]. Furthermore, other studies have reported many interesting results: the copper(II) complexes incorporating pyrazine analogs as bridging ligands, studied by proton magnetic resonance (PMR) and electron spin resonance (ESR) [20]; the thermochemistry of transition-metal M(pyrazine)$_2$Cl$_2$ complexes [21]; complexes formed by cobalt(II) halides with pyrazine [22]; the crystal structure and magnetic behavior of the cyanide-bridged dinuclear systems containing pyrazine [23]; the coordination complexes of functionalized pyrazines with metal ions as reagents for the flavorant molecules [24]; the complexes of tetramethylpyrazine with two serum albumins and layered coordination polymer of silver methanesulfonate described by Cheng [25] and Kokunov *et al.* [26], respectively; the synthesis, structure and fluorescence of cadmium(II) coordination polymers with derivatives of pyrazine-1,4-dioxide and thiocyanate [27]; the structure of 1:2 tetramethylpyrazine complex with 2,4,6-triiodophenol [28]; and the physiological and pharmaceutical effects of simple alkyl- and aryl-pyrazines described in a review by Ohta and Yamada [29].

We first studied the complexes of methyl derivatives of pyrazine with the strong proton donors chloranilic acid (CLA) and squaric acid (H_2SQ). In our previous review [1] we reported that both CLA and H_2SQ are important components in supramolecular chemistry and crystal engineering; they possess two proton donor and two proton acceptor groups, and exhibit electron donor properties. Thus, the hydrogen-bonded complexes with CLA and H_2SQ can be treated as EDA units.

In another review [30] we focused on CLA complexes with pyrazine and 1,2-diazine [31], and with pyrazole and imidazole [32]. Studies have shown that CLA forms complexes with pyrimidine and pyrazine, which form bifurcated hydrogen bridges [33]. Interesting complexes obtained with derivatives of bipyridils forming supramolecular architectures are also described in the papers of Zaman *et al.* [34-36]. The role of CLA as a component of the electron transfer reaction in biological systems was widely investigated in [37-39]. It is also possible to use CLA in analytical chemistry for the determination of traces of tungsten [40] and as the negative active material of alkaline batteries [41].

As will be shown in the present review, CLA forms complexes with methyl derivatives of pyrazine, particularly with tetramethylpyrazine [42-45]. CLA also forms an interesting complex with 4,4'-di-t-butyl-2,2'-bipyridyl, which shows antiferroelectric properties [46].

The crystal of H_2SQ exhibits polar properties, since its molecules in crystal lattices form layers containing hydrogen bonds [47-50]. Above 374 K in the paraelectric phase the compound is characterized by disordered protons, while below this temperature it is an ordered system (ferroelectric phase). H_2SQ shows the ability to form interesting structures with proton acceptors, as reported by Gilli *et al.* in a review of supramolecular architectures [51]. H_2SQ can form interesting structures in complex with compounds such as 4,4'-dipyridyl acetylene and 1,2-bis(4-pyridyl)ethylene [52], as well as with a number of

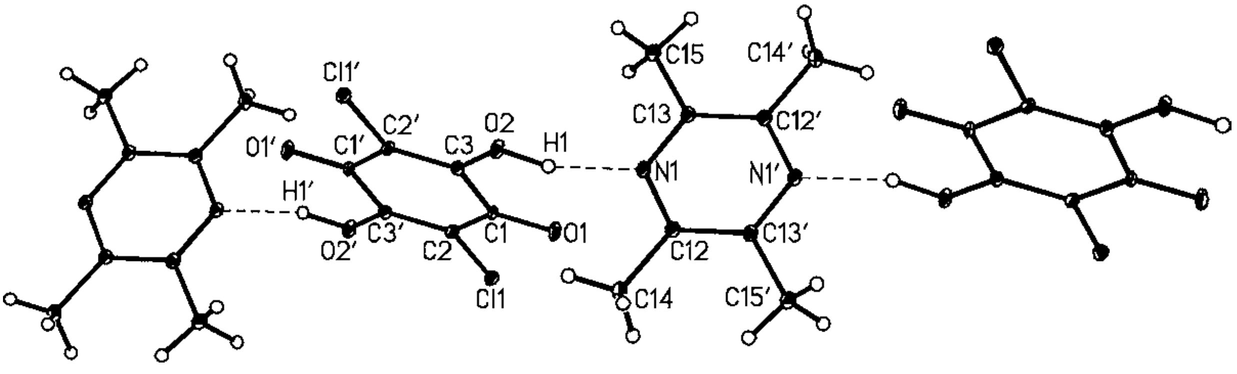

Fig. 1. Hydrogen bonded chains formed by TMP and CLA seen along the ***a***-axis in crystalline state. (Reproduced from Bator, G. and Sobczyk, L. 2011, Wiad. Chem., 65, 869 with permission from Wiadomosci Chemiczne).

nitric bases [53] and the proton sponge, 1,8-bis-dimethylaminomethyl naphthalene [54]. One report focused on the structure and magnetic properties of the H_2SQ complex with *p*-pyridyl-nitronylnitroxide revealing other interesting properties of these types of crystals [55]. H_2SQ was also used for complex-formation with 4-metoxypyridinium betaine, which revealed an order-disorder phase transition [56]. H_2SQ in complex with tetramethylpyrazine (TMP) will be discussed in the following section.

Preparation and structure of selected H-bonded complexes

Of all the complexes that have been investigated, the first one that should be discussed is the complex of TMP with CLA, which crystallizes from a 1:1 solution in acetonitrile [30]. In the crystalline lattice, the infinite chains of equivalent O-H···N hydrogen bonds are elongated along the c-axis as shown in Fig. 1 [30, 42]. The TMP and CLA rings are oriented with each other by an angle of 84.4^{o} as shown in Fig. 2.

Detailed studies on the effect of temperature and isotope substitution on the structure and crystal packing of the complexes have been reported in [43]. It has been established that at temperatures below 82 K a phase transition takes place, manifested by a doubling of the unit cells with alternation of the neighboring O-H···N hydrogen bonds. At a temperature of 14 K the lengths of the O-H···N bridges are equal to 2.668 and 2.714 Å. Deuteration led to an elongation of the O-H···N bridges by 0.022 Å, due to the Ubbelohde effect.

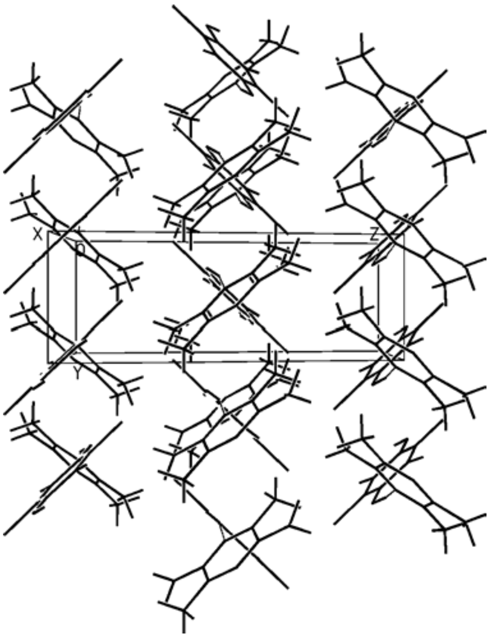

Fig. 2. Packing of TMP•CLA complexes in crystalline state seen along the a-axis. (Reproduced from Bator, G. and Sobczyk, L. 2011, Wiad. Chem., 65, 869 with permission from Wiadomosci Chemiczne).

In an earlier work we have shown that the H_2SQ•TMP complex crystallizes from an equimolar solution of acetonitrile-acetone mixture by slow cooling [47]. The rarely observed structure of this complex is shown in Fig. 3.

In the crystal lattice of monoprotonated TMP, the molecules form $^{+}$N-H···O^{-} hydrogen bonds with the ionized H_2SQ molecules (after deprotonation), which

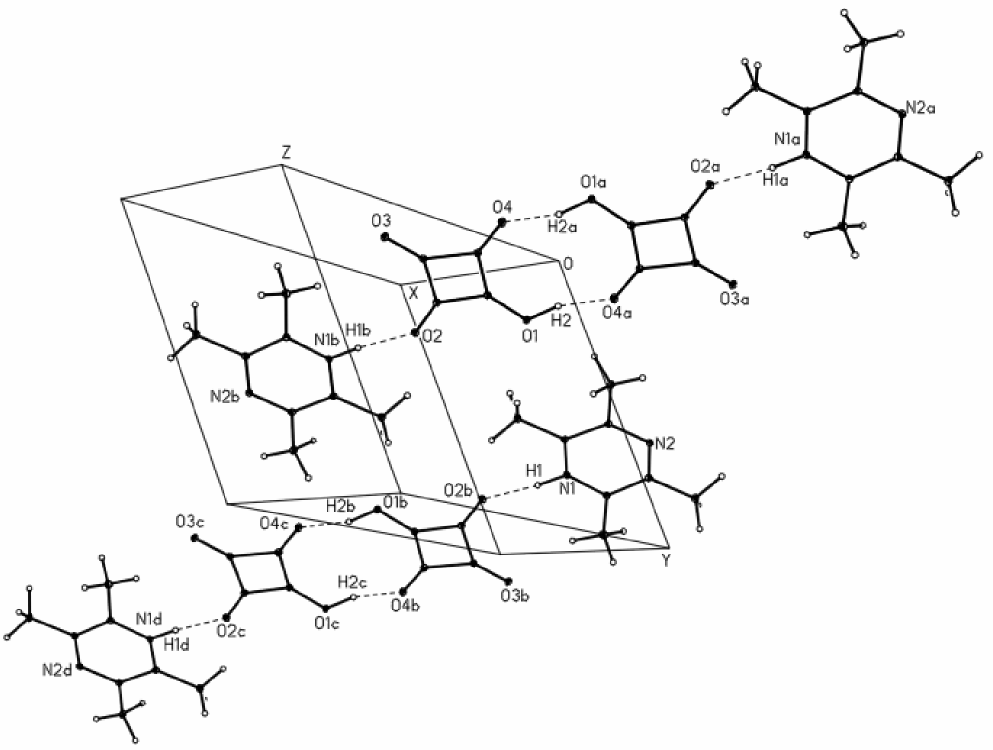

Fig. 3. Structural units of TMP•H_2SQ complexes and their packing in crystals. (Reproduced from Bator, G. and Sobczyk, L. 2011, Wiad. Chem., 65, 869 with permission from Wiadomosci Chemiczne).

in turn dimerize to form $[HSQ]_2^{-2}$•2TMPH$^+$ aggregations. The rings of H_2SQ and TMP are coplanar. The angles between the C-C bonds of HSQ^- anions are close to 90°, while the carbonyl oxygen atoms are oriented along the diagonals of the squaric rings. The protonated TMP rings preserve the symmetry plane oriented along the N···N axis. The contacts between TMP•H^+ cations take the form of the non-conventional C-H···N hydrogen bonds.

In addition to the formation of the H_2SQ•TMP complex, TMP complexes can also be formed with either picric acid or hydrogen triiodide (HI_3). The TMP•picric acid complex is prepared by mixing TMP with picric acid at a molar ratio of 1:2 in methanol. Single crystals are grown by slow evaporation at room temperature. In the case of the 1:2 TMP•picric acid complex, the protonation of both nitrogen atoms takes place as shown in Fig. 4 [57].

The TMP•H_2^{2+} cation is attached from both sides by picrate anions, which are crystallographically equivalent. The length of equivalent $^+NH\cdots O^-$ bridges equals 2.602 Å, which means that very strong hydrogen bonds are formed. In the case of TMP complexes with hydrogen triiodide, units composed of (TMP•$H^+)_2$ TMP cations and two triiodide anions are formed. As a result we obtain a cation containing three molecules, one TMP molecule with two $^+N\text{-}H\cdots N$ bridges and two monoprotonated TMP•H^+ molecules. The resulting structure is illustrated in Fig. 5 [58].

Based on the length of hydrogen bridges, which at room temperature is 2.874 Å, one can estimate that these hydrogen bonds are weak. In our earlier work, dark brown crystals of the [TMP•$H^+]_2$•TMP $(I_3^-)_2$ complex were prepared in a chloroform solution of TMP by adding, dropwise, a 40% aqueous solution of HI_3 to obtain the HI_3:TMP ratio equal to *ca.* 2:1 [58]. The crystalline complex of 2,5-dimethylpyrazine (2,5-DMP) with chloranilic acid was obtained by slow evaporation of acetone from a solution with 1:1 composition [59]. Complexation of components takes place,

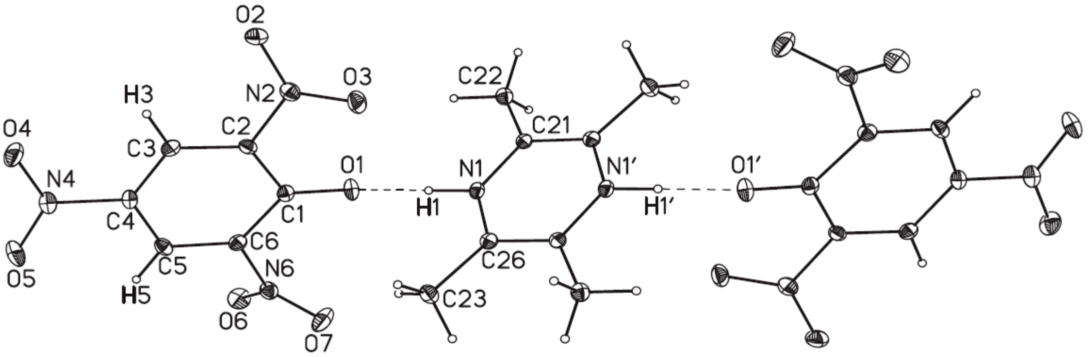

Fig. 4. Structure of 1:2 complexes formed by TMP and picric acid. (Reproduced from Bator, G. and Sobczyk, L. 2011, Wiad. Chem., 65, 869 with permission from Wiadomosci Chemiczne).

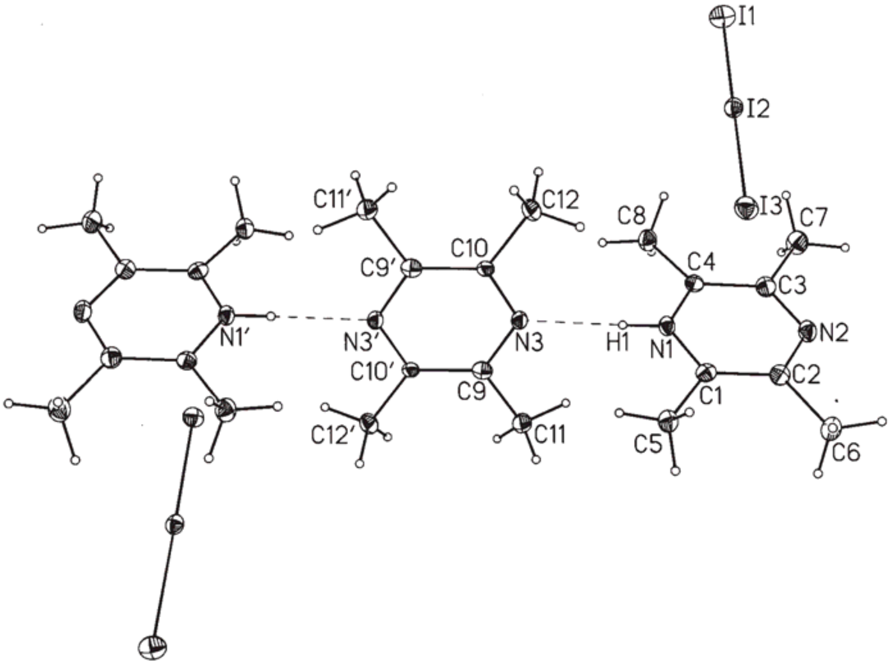

Fig. 5. The $(TMP{\cdot}H^{+})_2$ TMP cations and two triiodide anions in TMP complexes with hydrogen triiodide. (Reproduced from Bator, G. and Sobczyk, L. 2011, Wiad. Chem., 65, 869 with permission from Wiadomosci Chemiczne).

similar to the case of TMP•CLA, such that a chain of the O-H···N hydrogen bonds is extended along the *c*-axis. However, due to the presence of the C-H groups in 2,5-DMP, the packing of molecules in the crystal lattice is somewhat different; this packing is shown in Fig. 6 [59].

The crystalline complex of 2,6-dimethylpyrazine (2,6-DMP) was prepared in our earlier work [60] in a similar manner as that of 2,5-DMP with CLA [61]. The crystals of 2,6-DMP•CLA, which are similar to those containing 2,5-DMP, consist of chains built alternately by components along the *c*-axis. The crystal packing of these molecules is shown in Fig. 7 [61]. Some selected properties of the complex are discussed in a report by Pawlukojć *et al.* [60].

Recently, we investigated the complexation of TMP with nitric acid. This complex crystallizes

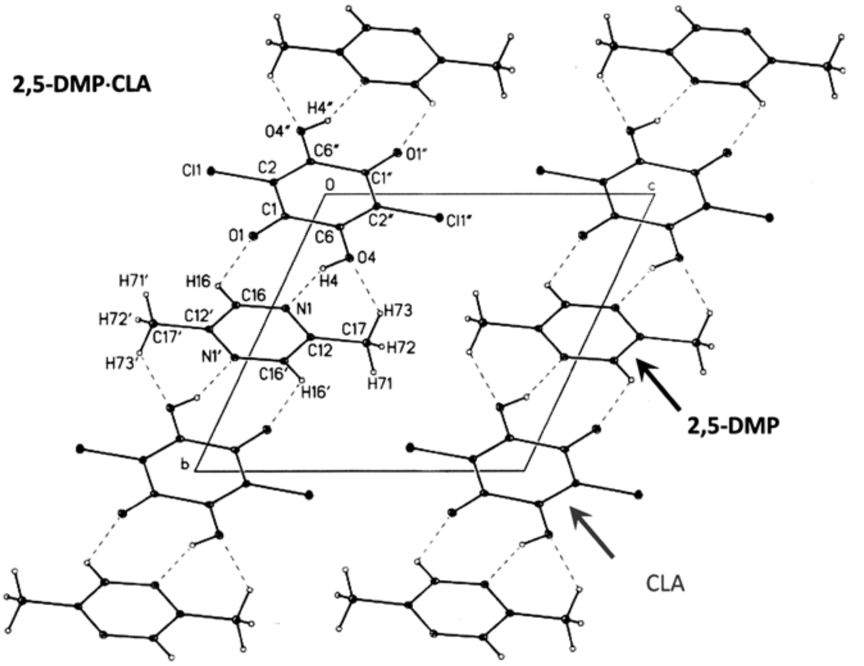

Fig. 6. Packing of 2,5-DMP•CLA complexes seen along the a-axis. (Modified from [59]).

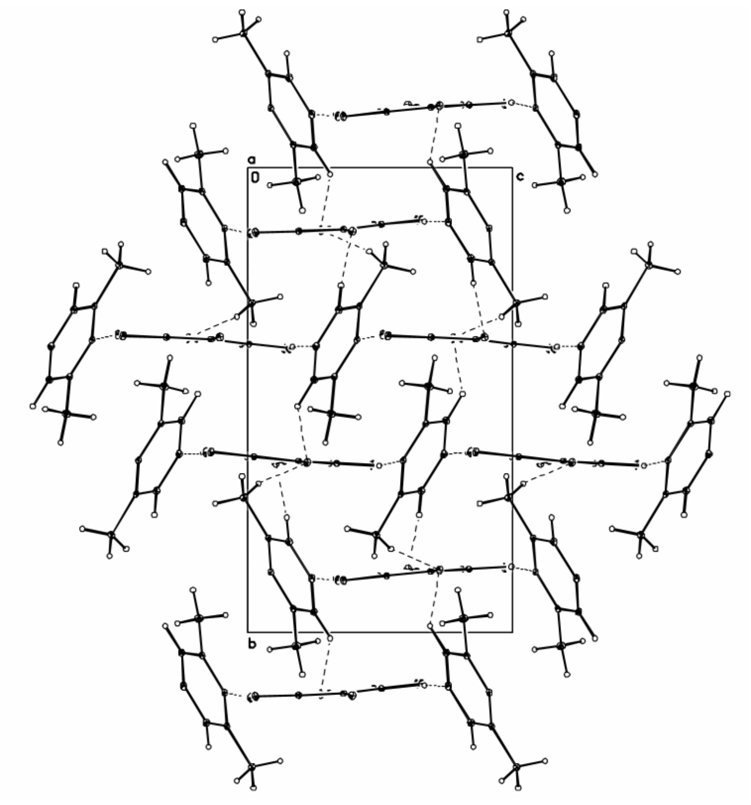

Fig. 7. Packing of 2,6-DMP•CLA complexes seen along the a-axis. (Reproduced from Bator, G. and Sobczyk, L. 2011, Wiad. Chem., 65, 869 with permission from Wiadomosci Chemiczne).

readily from acetonitrile in the hydrated form with two water molecules [62]. As shown in Fig. 8, the units consisting of the protonated TMP molecule and the NO_3^- anion are present in the crystal lattice, along with two water molecules bridging the ions.

Dehydration of the complex by dissolution in a less-active solvent leads to complicated aggregations.

Vibrational spectra

Since the complexes investigated by us contain strong hydrogen bonds, the appearance of intense continua in their infrared absorption spectra is expected and this ought to be observed for molecular complexes either with or without proton transfer. The best characteristic example is the TMP•CLA complex [30], the spectrum of which is shown in Fig. 9. An essential feature of the spectrum is the appearance of three absorption domains defined as the Hadži's trio, which is best characterized and defined in a report by Hadži and Bratos [63].

The observation can be interpreted quantitatively by assuming asymmetric potential for the proton motion in hydrogen bonds with two minima, according to the equation presented below [64]:

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

where r represents the coordinate of proton motion, and R is the coordinate of the bridge vibrations. The coefficients a_2, a_3 and a_4 are parameters dependent on R. The Hadži's trio results from the coupling of the anharmonic stretching vibration of the bridge proton with the vibrations of the bridge itself, which are damped due to the interaction with phonons. In the stochastic model presented in [65, 66] we deal with quasi-statistical distribution of the hydrogen bond lengths.

The absorption picture observed in the analysis of the TMP•CLA complex was compared with the results of the calculations for an asymmetric O-H-O bridge of 2.60 Å length presented in [67, 68]. In addition, in the TMP•CLA complex analyzed, the bridge length is equal to 2.65 Å. Therefore, one can interpret the observed infrared spectrum of the TMP•CLA complex in such a way that the band in the range 1100 cm^{-1} corresponds to the $0 \rightarrow 1$ transition and the band around 1900 cm^{-1} to the $1 \rightarrow 2$ transition, while the band at 2750 cm^{-1} corresponds to the $0 \rightarrow 2$ transition. According to the prediction, the band at 1900 cm^{-1} should be characterized by a low intensity [68]. This interpretation of the TMP•CLA spectrum does not exclude some additional effects connected with the Fermi resonance.

The structure of the TMP•H_2SQ complex is described by Nowicka-Scheibe *et al.* [47]. It was observed that in the crystal lattice both the anionic $(HSQ^-)_2$ dimers with strong O-H···O=C hydrogen bonds and the $^+$N-H···O^- bridges between the

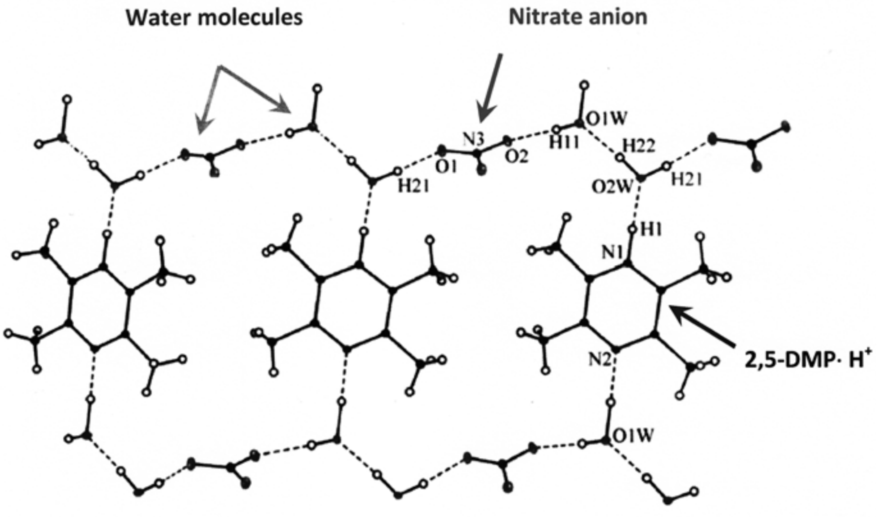

Fig. 8. Molecular structure of TMP nitrate dihydrate seen along the ***b***-axis. (Modified from [62]).

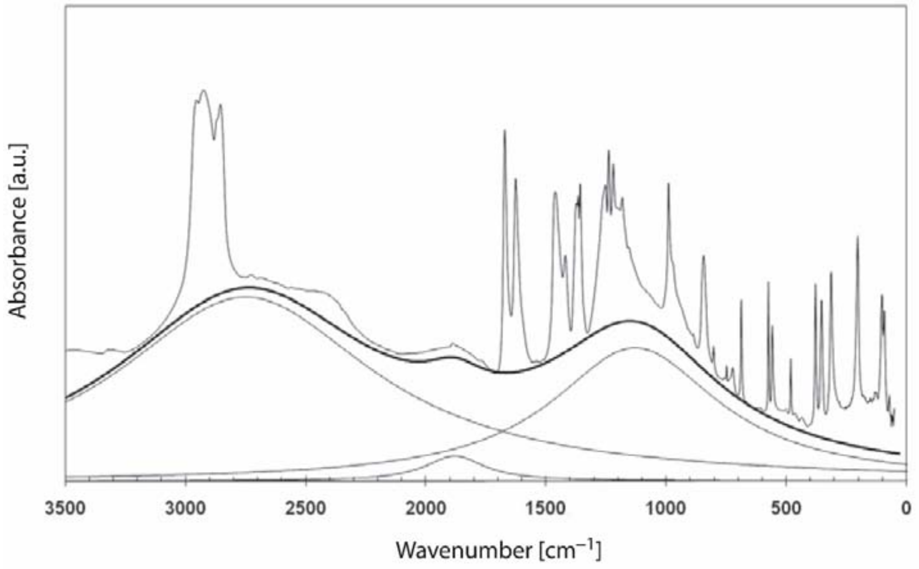

Fig. 9. Infra-red spectrum of TMP•CLA complexes in Nujol. (Reproduced from Bator, G. and Sobczyk, L. 2011, Wiad. Chem., 65, 869 with permission from Wiadomosci Chemiczne).

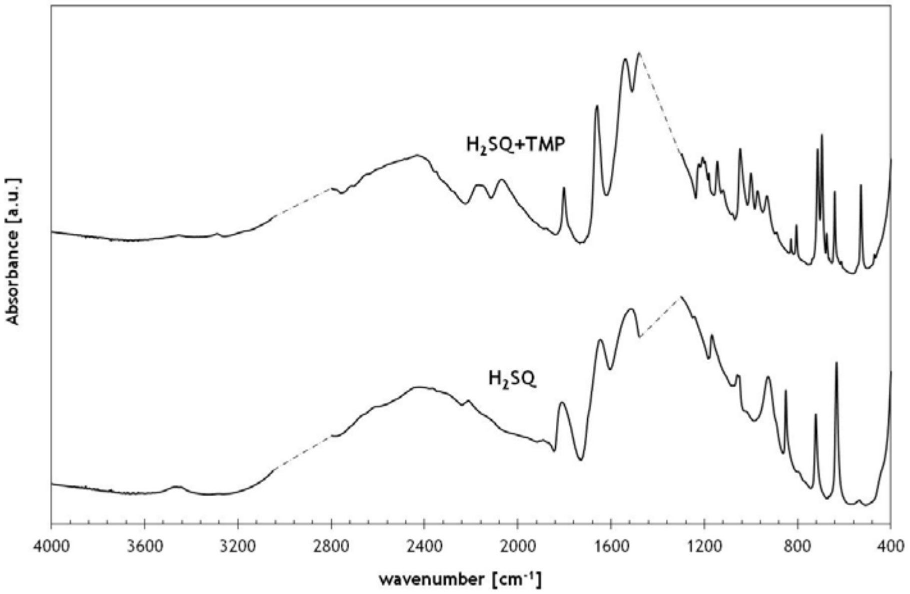

Fig. 10. Infra-red spectra of H_2SQ and that of its complex with TMP. (Modified from [47]).

complex components are formed. Fig. 10 shows the comparison of the infrared spectra of H_2SQ alone and that of its complex with TMP [47].

The similarity between the infrared spectra of these complexes is well established. This observation confirms the presence of a single asymmetric energy minimum in both cases, as shown by Denisov *et al.* [69]. The question arises as to the localization of the band assigned to the $^+$N–H stretching vibrations. It seems that the lack of such a band is due to its overlapping with a continuum arising from the O-H···O=C vibrations. The origin of the doublet at 2069 and 2176 cm^{-1} is also questionable. Perhaps this doublet is the result of the overtone and summation modes of the -CH_3 deformation vibrations. Comparison of the ν(C=O) vibration bands at 1660 and 1803 cm^{-1} for the complex and neat H_2SQ reveals no difference in position of these bands. A greater broadness in neat H_2SQ bands can arise from a lattice that is less rigid, leading to an increase in the role of librational modes.

Recently, we have studied the spectrum of the nitric acid•TMP complex, which crystallizes in the dihydrated form. The infrared spectrum of dihydrated TMP nitrate measured in Fluorolube is presented in Fig. 11 [62].

The doublet at high frequencies with maxima at 3342 and 3250 cm^{-1} can be ascribed to the OH stretching vibrations: asymmetric ν_{as}(OH) and symmetric ν_s(OH). The position of this doublet indicates weak hydrogen bonds. It seems that $^+$N-H···OH_2 vibrations correspond to the broad band at *ca*. 2485 cm^{-1}. Below this band a relatively weak doublet (above 2000 cm^{-1}) appears, the nature of which is not clear. Most likely it is due to the Fermi resonance between the hydrogen vibration in the $^+$N–H···OH_2 bridge and skeletal vibrations of the TMP molecule. The intense band at *ca*. 1300 cm^{-1}, with a few submaxima, probably results from the overlapping of a number of -CH_3 bending modes.

Neutron scattering phenomena and dynamics of methyl groups

The most important technique we used [42, 43, 45, 46, 60, 61, 70, 71] to determine methyl group dynamics in molecular complexes involved neutron scattering. The parameters of the -CH_3 rotational potential can be estimated by combined neutron backscattering and time-of-flight experiments, from which we derived (*i*) the tunneling splitting at low temperature, (*ii*) the jump-diffusional rotation rate at moderate temperature (Quasielastic Neutron Scattering [QENS]), and (*iii*) the torsional energy (Inelastic Neutron Scattering [INS]).

In the solid state of molecular complexes containing tetramethylpyrazine, two effects influence the rotational potential of the methyl groups: the charge transfer or hydrogen bond formation, and the packing of the crystal lattice. The decrease in the electron density in the aromatic ring of the molecule causes a decrease of the -CH_3 rotational barrier. In contrast, the steric hindrance, which naturally appears in the crystal lattice, results in an increase of the barrier. For several years the quantitative determination of these two competing contributions has been the subject of our systematic studies [42, 43, 45, 46, 60, 61, 70, 71] on systems that have a different degree of charge transfer and/or different

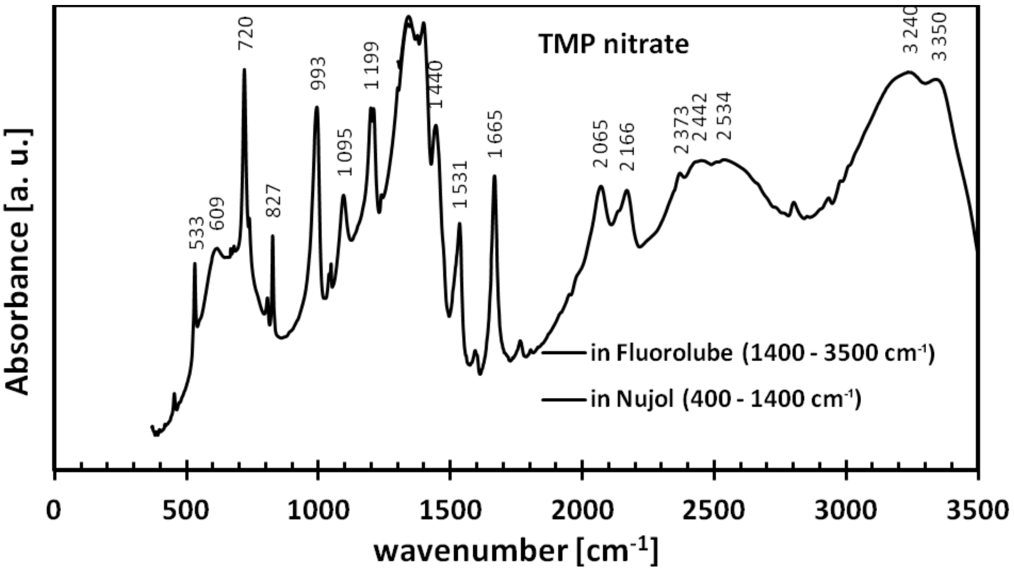

Fig. 11. Infra-red spectrum of dihydrated TMP nitrate. (Modified from [62]).

hydrogen bond strength (with or without proton transfer). Moreover, the complexes crystallize in different crystal systems, the effect of which cannot be neglected.

Tunneling spectroscopy is an extremely sensitive probe of local potentials. The estimation of the potential parameters of the -CH_3 rotations in the solid state have already been carried out for some molecular complexes of tetramethylpyrazine. The complex of TMP•CLA was first measured with the backscattering spectrometer (BSS) of Forschungszentrum Jülich by Prager *et al.* [42, 43]. The preliminary results showed that at least three tunneling peaks could be distinguished. We re-examined these measurements using the third-generation instrument SPHERES, which has high resolution and seemed ideally suited to verify the tunneling splitting observed in Jülich.

TMP in complex with bromanilic acid (BRA) was compared with that containing chloranilic acid, TMP•CLA [71]. The crystal structures of both TMP•CLA and TMP•BRA were determined by us. The crystal structure of TMP•BRA is described in [71], whereas that of TMP•CLA is described in detail by Prager *et al.* [43] and Sawka-Dobrowolska *et al.* [30]. The knowledge of both crystal structures was necessary in order to determine the number of inequivalent methyl groups in the TMP•BRA crystal structure. This, in turn, resulted in the determination of the number of expected tunneling peaks in the INS spectra.

Unexpectedly, no tunneling band was observed for the TMP•BRA complex, probably due to the position of bands outside the available energy window for the experiment. This is undoubtedly due to a different crystal structure compared to that of TMP•CLA. In the case of TMP•CLA, we observed four tunneling bands as shown in Fig. 12 and in Table 1 (at 3 K: ± 2.2, ± 3.7, ± 22 and ± 31 μeV [71]).

Other complexes for which tunneling splitting have been investigated are: TMP•PA (PA – picric acid) [57], TMP•PNP (PNP – paranitrophenol,) [70], and the complexes of methyl-substituted bipyridyls with CLA [46]. All the compounds showed tunneling splitting and the tunneling parameters were estimated and cited in [57, 70, 46].

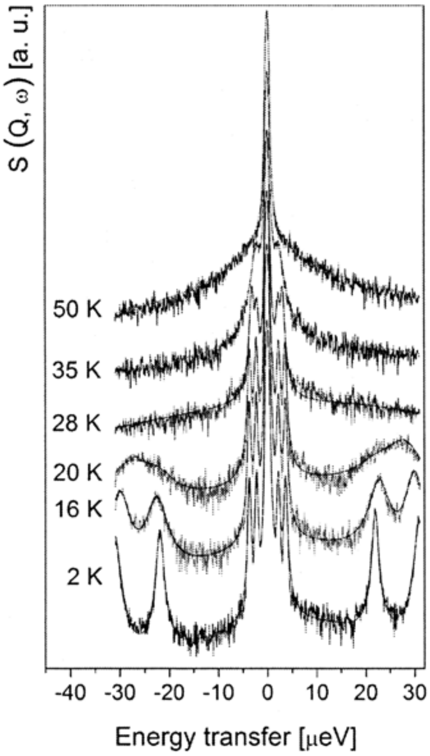

Fig. 12. The tunneling spectra of TMP•CLA at several temperatures between 3.0 and 50 K measured with SPHERE. (Modified from [71]).

Table 1. The tunneling transitions and activation energies of quasielastic scattering for TMP and TMP•CLA complex. The values in bracket are estimated based on the best fit to E_{01}.

	$\hbar\omega_t$	E_{01}
TMP	(μeV)	(meV)
	(0.02)	22.0
	(0.001)	23.6
TMP•CLA	2.2	14.6
	3.7	
	22	11.0
	31	9.9

QENS yields information on the stochastic scattering resulting from methyl groups present in the crystal structure at moderate temperatures. Prager *et al.* observed the QENS signals at temperatures between 40 and 140 K [43]. Table 1

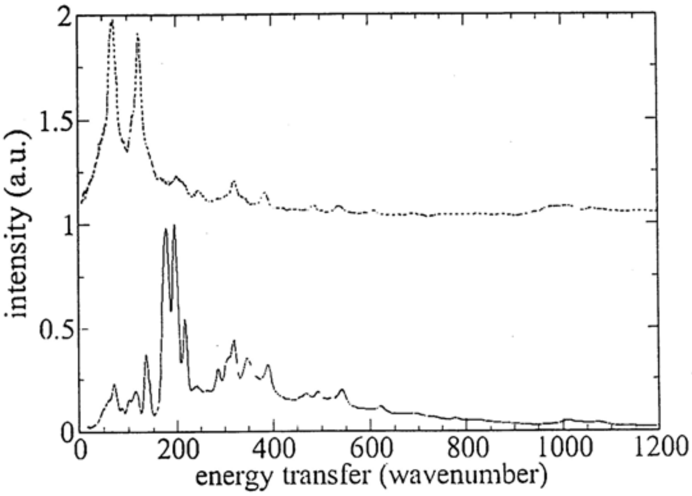

Fig. 13. INS spectra of TMP and TMP•CLA. (Reproduced from Bator, G. and Sobczyk, L. 2011, Wiad. Chem., 65, 869 with permission from Wiadomosci Chemiczne).

Table 2. Experimental energies of INS bands for TMP and TMP•CLA compared with calculated values for isolated TMP molecules.

		Experimental INS		Calculated
		TMP	TMP•CLA	B3LYP/6-31G(d,p)
$CH_{3\ \mathrm{tors}}$	{	171	68	120
		171	74	122
		190	122	140
		190	124	156

shows the tunneling transitions and activation energies of quasielastic scattering for both the neat TMP and the TMP•CLA complex. Fig. 13 shows the INS spectra at energies corresponding to the internal vibrations for TMP and TMP•CLA. We observed very intense bands assigned to the -CH_3 torsional vibrations and particularly low values of their energy transfer. Calculated values, obtained by means of the DFT/B3LYP/6-31(d,p) method as applied to the isolated molecule, are shown in Table 2.

The experimental results obtained using inelastic and quasielastic neutron scattering allowed us to draw a conclusion about the methyl group rotations in the crystal lattice. The -CH_3 groups rotate more freely when the TMP molecule forms a molecular complex in the solid state than when TMP molecules alone form a crystal. It appears that crystal packing plays a decisive role in the effect on the energy barrier value for methyl group rotations.

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CONFLICT OF INTEREST STATEMENT

The authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest (such as honoraria, educational grants, participation in speakers' bureaus, membership, employment, consultancies, stock ownership, or other equity interest, and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

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