

Interaction Products in the System Sulfur Dioxide–2,2'-Bipyridine–Water. Van der Waals Clathrates

R. E. Khoma^{a,b*}, V. O. Gelmboldt^c, A. A. Ennan^a, V. N. Baumer^{d,e}, and M. D. Tsapko^f

^a Physicochemical Institute for Environmental and Human Protection, Ministry of Education and Science and National Academy of Sciences of Ukraine, ul. Preobrazhenskaya 3, Odessa, 65082 Ukraine

*e-mail: rek@onu.edu.ua

^b Mechnikov Odessa National University, Dvoryanskaya ul. 2, Odessa, 65082 Ukraine

^c Odessa National Medical University, Valikhovskii per. 2, Odessa, 65082 Ukraine

^d Institute for Single Crystals, National Academy of Sciences of Ukraine, pr. Lenina 60, Kharkiv, 61001 Ukraine

^e Karazin Kharkiv National University, Kharkov, pl. Svobody 4, Kharkiv, 61022 Ukraine

^f Taras Shevchenko National University of Kyiv, Vladimirskaya ul. 60, Kyiv, 01033 Ukraine

Received April 21, 2016

Abstract—Crystallization of 2,2'-bipyridine from aqueous solution containing sulfur(IV) oxide afforded clathrates with the composition $(\text{bipy})_k \cdot (\text{SO}_2)_m \cdot (\text{H}_2\text{O})_n$. X-Ray amorphous guest SO_2 molecules occupy voids in the crystal lattice of 2,2'-bipyridine without distortion of its structure. The isolated compounds were characterized by elemental analyses, X-ray diffraction data, and IR, NMR, and mass spectra.

Keywords: 2,2'-bipyridine, sulfur(IV) oxide, aqueous solution, van der Waals clathrates

DOI: 10.1134/S1070363216090097

2,2'-Bipyridine (bipy) and its derivatives and salts constitute structural fragments of alkaloids; they are used as analytical reagents, dyes in textile industry, anti-oxidants, and herbicides and are promising materials for non-linear optics [1–3]. 2,2'-Bipyridine forms colored complexes with metal salts, S_2Cl_2 , SO_3 , organic halides, phenols, and amines [3]. The structure of bipy was studied in [4, 5]. It reacts with mineral acids to give ionic salts via mono- [6–8] and diprotonation [9–13], whereas its salts with organic acids are molecular H-bonded adducts [14, 15].

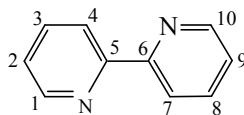
It is known that reactions of sulfur(IV) oxide with various organic bases (2-aminoethanols [16–19], di- and polyamines [20–22], alkylamines [21, 23], amino-guanidine [24]) in water are accompanied by salt formation and that its reactions with amides (thioamides) [25–28] involve hydrolysis and condensation processes leading to various molecular and ionic products. Examples of clathrate compounds with SO_2 as guest molecules have been reported [29–31].

In this work we have isolated and studied crystalline products with the compositions $(\text{SO}_2) \cdot (\text{bipy})_3 \cdot (\text{H}_2\text{O})$

(**1**) and $(\text{SO}_2) \cdot (\text{bipy})_2 \cdot (\text{H}_2\text{O})_2$ (**2**). Before proceeding with the discussion of our results, it should be noted that the fragmentation patterns of bipy in the mass spectra of **1** and **2** are in a good agreement with previously published data [32].

According to the ^1H NMR data (DMSO- d_6 , 400 MHz), signals of all aromatic protons in the spectra of **1** and **2** appear in a weaker field relative to those in the spectrum of bipy due to acceptor effect of SO_2 (Table 1). Analogous pattern was observed for the anionic complex $[\text{Au}(\text{bipy})\text{Cl}_2]^-$ [33]. The SO_2 –bipy ratio in **2** is higher than in **1**. Obviously, this is the reason why the electron density on the nitrogen atoms in **2** is lower than in **1** (Table 1). There is no protonation of the nitrogen atoms.

In the ^{13}C NMR spectra (DMSO- d_6 , 100 MHz) of **1** and **2**, signals from C^2 – C^4 and C^7 – C^9 are displaced downfield. The electron density on the other carbons unexpectedly increases, as was observed for the anionic Au(III) complex with bipy [33]. The upfield or downfield shift of the above signals increases in parallel with the concentration of SO_2 and H_2O in the clathrates.

Table 1. ^1H and ^{13}C NMR spectra of 2,2'-bipyridine and clathrates **1** and **2** in $\text{DMSO-}d_6$ 

Position	δ , ppm (J , Hz)			δ_{C} , ppm (J , Hz)		
	bipy	1	2	bipy	1	2
1.1	8.68 d ($J=3.7$)	8.71 d ($J=4.3$)	8.74 s	149.24	148.9	148.33
4.7	8.39 d ($J=7.9$)	8.43 d ($J=7.9$)	8.45 d ($J=7.3$)	120.40	120.8	121.68
3.8	7.93 t ($J=7.3$)	8.02 t ($J=7.3$)	8.09 t ($J=7.3$)	137.27	139.95	139.38
2.9	7.44 t ($J=5.5$)	7.52 t ($J=4.3$)	7.59 s	124.16	124.5	125.34
5.6	–	–	–	155.10	154.37	152.35

Table 2 shows the results of analysis of the IR spectra of bipy and compounds **1** and **2**. Vibration frequencies were assigned on the basis of the data of [34]. Characteristic $\nu(\text{C}_{\text{arom}}\text{-H})$ bands of bipy were observed in the region $3100\text{--}3000\text{ cm}^{-1}$. Taking into account C_{2v} symmetry of the bipy molecule, eight C–H stretchings (four A_1 and for B_2) are active in the IR spectrum [34]. The position of these bands in the spectra of **1** and **2** is almost the same as in the spectrum of free bipy.

Benzene-type aromatic compounds are characterized by four vibrations of the benzene ring with their frequencies ranging from 1600 to 1300 cm^{-1} . Uncoordinated bipy also shows four bands in that region, at 1579 , 1558 , 1452 , and 1415 cm^{-1} (Table 2) [35]. Bands corresponding to C=C and C=N stretchings ($1600\text{--}1400\text{ cm}^{-1}$) are sensitive to chelation [35], which promotes isomerization of bipy from *trans* configuration [4] in the free state to *cis* [6–8, 33–36]. The formation of **1** and **2** is accompanied by low-frequency shift of the ring stretching bands by 4 and 6 cm^{-1} , respectively. The position of the other bands remains unchanged.

Absorption bands at 1040 and 991 cm^{-1} of free bipy may be assigned to breathing vibrations of the ring and out-of-plane bending vibrations of the C–H bonds, respectively. The first band in the spectra of **1** and **2** is observed at the same position, while the second band is shifted to higher frequencies (995 and 993 cm^{-1} for **1** and **2**, respectively). This shift indicates participation of C–H protons in weak interactions and is consistent with the NMR data.

It is known [37] that isolated SO_2 molecule belongs to C_{2v} point group symmetry and is characterized by three main vibrational frequencies: ν_1 (A_1 , S=O,

symmetric stretching), ν_2 (A_1 , O=S=O, bending), and ν_3 (B_1 , S=O, asymmetric stretching). These vibrations appear in the ranges ν_2 $596\text{--}553\text{ cm}^{-1}$, ν_1 $1190\text{--}1153\text{ cm}^{-1}$, and ν_3 $1356\text{--}1280\text{ cm}^{-1}$; the band at $2513\text{--}2467\text{ cm}^{-1}$ is an overtone band; the ν_2 frequency of $\text{SO}_{2(\text{s})}$ at room temperature is 552 cm^{-1} (this value was obtained by extrapolation) [37].

The absorption bands at 552 and 551 cm^{-1} in the IR spectra of **1** and **2**, respectively, correspond to ν_2 bending vibrations of SO_2 . The ν_1 stretchings appear at 1158 cm^{-1} in the spectra of both products; similar frequency is also typical of aqueous solution of SO_2 at -10°C (1151 cm^{-1}) [30].

The ν_3 mode with its maxima (B_1 , B_2) [38] at 1314 (w) and 1321 cm^{-1} (m) is observed in the IR spectrum of **1**, and compound **2** displayed ν_3 bands at 1312 (w) and 1323 cm^{-1} (sh, w). This region of the spectrum also contained bands at 1375 (m) and 1279 cm^{-1} (w) for **1** and two weak doublets at $1362/1336$ and $1295/1280\text{ cm}^{-1}$ and a shoulder at 1375 cm^{-1} for **2**. The ν_3 frequency of $\text{SO}_{2(\text{g})}$ and $\text{SO}_{2(\text{s})}$ (78 K) is 1362 and 1322 cm^{-1} , respectively; intermediate value 1336 cm^{-1} is typical of amorphous SO_2 agglomerates, and 1342 cm^{-1} , of SO_2 clathrate hydrate (at 263 K) [30].

Water in SO_2 clathrate hydrate (263 K) shows OH stretchings ν_1 and ν_3 (3400 cm^{-1}), bending ν_2 (1643 cm^{-1}), libration γ (667 cm^{-1}), and composite $\delta + \gamma$ (2143 cm^{-1}) [30]. Vibrations of water molecules (ν_1 , ν_3) in the spectrum of **1** are observed at 3230 (cf. $3240 \pm 20\text{ cm}^{-1}$ for SO_2 clathrate hydrate at 266 K [30]) and 3336 cm^{-1} (3400 cm^{-1} for aqueous solution of SO_2 at 263 K [30]). The corresponding vibrations appear in the spectrum of **2** at higher frequencies as a series of bands at 3851 , 3836 , 3819 , 3742 , 3733 , and 3673 cm^{-1} .