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Hydrogen bonding in coordination compounds containing homoconjugated bis-dimethylsulfoxide cation. Ab initio and IR studies

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Abstract

DFT calculations of vibrational spectra and structural parameters of dimethylsulfoxide (DMSO) molecule, its hydrogen bonded complex with HCl, mono- and bis-dimethylsulfoxide cations $DMSOH^+$ and $DMSOHOSDM^+$ have been performed at B3LYP/6-31G** level. The results obtained for free DMSO and DMSO + HCl complex are in good agreement with the known experimental data. For free homoconjugated cation $(DMSOHOSDM)^+$, an extremely short ($R_{O\cdots O} = 2.40$ Å) and a practically linear hydrogen bond with nearly central position of the bridging proton have been found. The addition of a counterion leads to lengthening and bending of the hydrogen bond. A solid $[(DMSO)_2H]_2[PtCl_6]$ compound has been synthesized and the IR spectrum of this salt has been investigated. The structural parameters and vibrational frequencies calculated for $[(DMSO)_2H]^+X^-$ complexes (X = Cl, BF_4) were found to be in good agreement with experimental X-rays and IR data for solid $[(DMSO)_2H]_2[PtCl_6]$. The most important feature of vibrational spectrum of homoconjugated bis-dimethylsulfoxide cation is the essential involvement of proton stretching and bending coordinates in different normal modes, resulting in mixing of proton vibrations with vibrations of sulfoxide moiety, particularly with νSO, νCS, δCH. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen bond; Homoconjugated cation; Vibrational spectrum; Dimethylsulfoxide

1. Introduction

The aim of this work is to study the structural and spectral peculiarities of compounds containing strongly hydrogen bonded dimethylsulfoxide molecule and its protonated forms, particularly homoconjugated bis-dimethylsulfoxide cation $(DMSO\cdots H\cdots OSDM)^+$. The reasons for our interest in this problem are as follows.

Dimethylsulfoxide is known to reveal a strong proton accepting ability when forming hydrogen bonded complexes with various proton donors. However, no reliable spectroscopic evidence of DMSO protonation with formation of $DMSOH^+$ monocation in solutions was obtained so far. No manifestations of the complete proton transfer were detected in the IR spectra of binary complexes formed

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Table 1
Vibrational modes of of Me_2SO and $Me_2SO\cdots HCl$ complex. Comparison of calculated frequencies (cm^{-1}) and intensities (in brackets, $km\ mol^{-1}$) with experimental data [3]

Me_2SO			$Me_2SO\cdots HCl$		
Calc.	Ar matrix [3]	Assignment	calc.	Ar matrix [3]	Assignment
			24		ν_γ
			56		ν_β
			156		ν_σ
184		CH_3 tors	181		CH_3 tors
232		CH_3 tors	229		CH_3 tors
283 (0.6)		CSC bend	293 (6)		CSC bend
296 (7)	328 m	CSO bend	296 (6)		γCSO, γOHCl
359 (7.5)	375 m	CSO bend	382 (55)	398 w	δCSO,δOHCl
			623 (33)	(612)	γClOH
633 (10)	654 m	CSC stretch	649 (11)		CSC stretch
662 (21)	680 s	CSC stretch	687 (18)	700	CSC stretch
			766 (83)	781 m	δOHCl
896 (2)	878 m	CH_3 rock	912 (3)	888 w	CH_3 rock
936 (6)	914 ms	CH_3 rock	952 (5)	922 w	CH_3 rock
965 (12)	941 m	CH_3 rock	969 (85)	946 w	CH_3 rock
1030 (22)	1008	CH_3 rock	1046 (26)		CH_3 rock
1100 (112)	1091 vs	ν S=O	1039 (216)	1032 m	ν S=O
1331 (0.7)	1295 w	CH_3 deform	1343 (0.7)		CH_3 deform
1355 (7)	1312 m	CH_3 deform	1368 (4)		CH_3 deform
1455 (9)	1404 ms	CH_3 deform	1455 (11)		CH_3 deform
1469 (3)	1417 m	CH_3 deform	1468 (5)		CH_3 deform
1473 (0.5)		CH_3 deform	1472 (0.3)		CH_3 deform
1491 (19)	1437 s	CH_3 deform	1490 (22)		CH_3 deform
			2264 (2385)	1251 s	νHCl

by DMSO with strong acids like CCl_3COOH, HBr, HI, HNO_3 in crystalline form [1,2] and in low temperature argon matrices [3,4].

A more stable protonated form of DMSO is bis-dimethylsulfoxide cation $(DMSO)_2H^+$. An additional interest in studying this ion is due to the fact that it represents an example of the system with strong and short symmetrical hydrogen bond. The formation of such a compound in liquid mixtures of DMSO with methanesulfonic acid was suggested for the first time by Williams and Kreevoy [5]. The suggestion was based on the presence of the broad intensive absorption in the low frequency part of the IR spectrum, typical for symmetrical $O\cdots H\cdots O$ bonds. Later, a similar conclusion was made in Ref. [6], where more detailed study of this system was performed using the ATR technique. No bands belonging to $(DMSO\cdots H\cdots OSDM)^+$ vibrations, other than $\nu(O\cdots H\cdots O)$, were found and assigned in Refs. [5,6].

Existence of $(DMSO\cdots H\cdots OSDM)^+$ cation in crystalline salts of some coordination compounds was proved by X-ray studies [7–10]. The appearance of some IR bands typical for such compounds was mentioned [9,10]. However, the whole IR spectrum of the cation was not presented and analyzed.

In the present work, DFT at B3LYP/6-31G** level, calculations of structure and vibrational spectra of DMSO, DMSO·HCl complex, $DMSOH^+$ and $(DMSO\cdots H\cdots OSDM)^+$ cations and ionic pairs $(DMSOHOSDM)^+X^-$, where $X = Cl$, BF_4 have been performed. Solid $[(DMSO)_2H]_2[PtCl_6]$ has been synthesized and its IR spectrum has been investigated.

2. Experimental

$[(DMSO)_2H]_2[PtCl_6]$ was synthesized using the method described in Ref. [10]. Infrared spectra of

Table 2
Structural parameters of bis-dimethylsulfoxide cation

	$[Me_2SO]_2H^+$ (calc.)	$[Me_2SO]_2H^+BF_4^-$ (calc.)	$[Me_2SO]_2H^+Cl^-$ (calc.)	$[(Me_2SO)_2H]_2[PtCl_6]$ X-ray data [12]
$R_{O\cdots O}$ (Å)	2.403	2.422	2.434	2.420
∠OHO (in degrees)	179.78	166.99	164.09	166.5[a]
R_{O1H} (Å)	1.195	1.106	1.085	1.219
R_{HO2} (Å)	1.208	1.331	1.372	1.267
R_{S1O1} (Å)	1.576	1.585	1.594	1.587
R_{S2O2} (Å)	1.574	1.562	1.557	1.563

[a] According to Ref. [14], a more exact value is 153.6°.

the samples pressed in KBr pellets were recorded with FT-IR Bruker IFS-28 spectrometer within the range 4000–400 cm^{-1}.

3. Calculations

The quantum mechanical calculations were performed using DFT method at B3LYP/6-31G** level, by GAUSSIAN 94 program [11]. No force field scaling was used to correct calculated frequencies.

4. Results and discussion

1. In the first stage, vibrational spectra of free DMSO molecule and strongly hydrogen bonded complex DMSO·HCl have been calculated. The comparison with experimental spectra in Ar matrices, obtained by Barnes et al. [3,4] (Table 1) shows that the approximation used for calculations allows to reproduce characteristics of vibrational modes of DMSO moiety with rather good accuracy. For the complex, the essential mixing of O···HCl bending movement with other modes is found. A significant disagreement is observed only for νHCl vibration in the complex. Obviously, the reason for such a disagreement is high anharmonicity of this vibration. According to Ref. [3], its frequency is very low (about 1250 cm^{-1}), hydrogen bond being extremely strong.

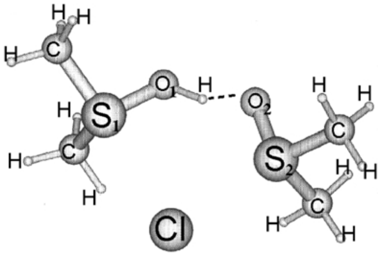

Fig. 1. 6-31 G** structure of bis-dimethylsulfoxide complex with Cl^-.

2. In the next stage structural data for free (isolated) bis-dimethylsulfoxide cation and its ionic pairs with Cl^- and BF_4^- anions were obtained.

For isolated homoconjugated cation, the extremely short ($R_{O\cdots O} = 2.403$ Å) and practically linear hydrogen bond with bridging proton located almost exactly in the center between two oxygen atoms have been found (Table 2). S–O distances are also equal. Thus this system can be considered as an example of a really symmetrical hydrogen bond with potential surface having the single minimum corresponding to the central position of the bridging proton.

The interaction with a counterion leads to lengthening (weakening) and bending of the hydrogen bond, proton shifts from O···O line towards the anion. Thus, one can speak about bifurcation of the hydrogen bond in such systems. The structure of $[DMSO]_2H^+$ complex with Cl^-, resulting from calculations, is shown in Fig. 1. One can see rather clearly the displacement of the proton towards Cl^-.

An important fact is also that $O_1\cdots H$ and $H\cdots O_2$, as well as S_1–O_1 and S_2–O_2 distances become essentially unequal due to interaction with an anion. It is noticeable that the perturbation of bis-dimethylsulfoxide cation's structure by the interaction with Cl^- is stronger than with BF_4^-. Particularly, O···O distance increases to 2.422 Å with BF_4^- anion and to 2.434 Å with Cl^-; ∠OHO angle decreases to ~167° in the

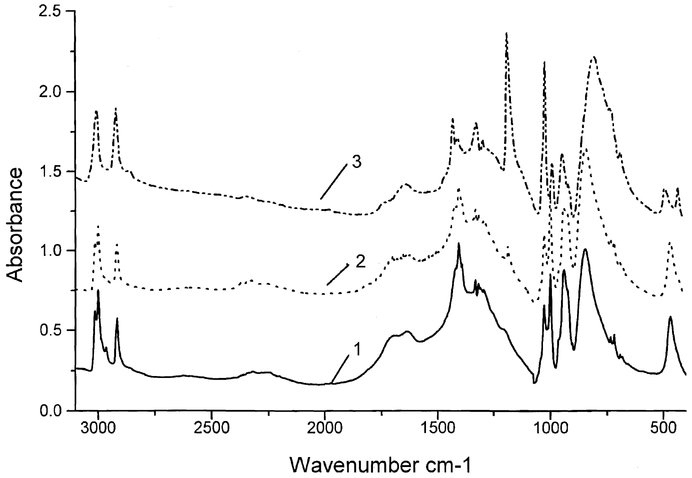

Fig. 2. Spectrum of $[(DMSO)_2H]_2PtCl_6$ in KBr: (1) initial sample; (2,3) changes with time.

case of BF_4^- and to ~164° in the case of Cl^-; the difference between the lengths of two OH and SO bonds increases from BF_4^- to Cl^-. This can be attributed to the larger size of the BF_4^- anion and hence lower surface density of the negative charge.

It is interesting to compare these results with the available X-ray data. It turned out that the calculated structural parameters are in a reasonable agreement with those reported for $[(DMSO)_2H]_2PtCl_6$ and some other related coordination compounds containing $(DMSO)_2H$ cation [10]. Particularly, Table 2 shows that the hydrogen bond in the real $[(DMSO)_2H]_2PtCl_6$ complex is very short indeed: O···O distance is 2.42 Å. It is longer than that calculated for free cation, shorter than that calculated for $[(DMSO)_2H]Cl$ and very close to the one calculated for $[(DMSO)_2H]BF_4$. The lengths of both SO bonds are almost equal to those obtained for $[(DMSO)_2H]BF_4$. This indicates that perturbation of O···H···O bond by Cl^- is stronger than by $PtCl_6^-$. The difference in the lengths of two OH bonds, calculated for model complexes, in both cases is bigger than that found for $[(DMSO)_2H]_2PtCl_6$, however the value of this difference in the case of BF_4^- complex is closer to the observed value. The experimental data confirm the essential nonlinearity of O···H···O bridge and the shift of proton position from the center of the bridge under influence of a counterion. According to Ref. [10], the angle ∠ OHO in different compounds varies from 146 to 173°. For $[(DMSO)_2H]_2PtCl_6$ a value of 166.5° is presented in Ref. [10]. However, recently a more precise value of 153.6° has been communicated [12]. The reason for the difference between experimental and calculated values of the angle seems to be connected with peculiarities of the crystalline lattice of $[(DMSO)_2H]_2PtCl_6$.

3. Experimental IR spectrum of solid $[(DMSO)_2H]_2[PtCl_6]$ pressed in KBr pellet is presented in Fig. 2, curve 1. This spectrum differs strongly from spectra of typical complexes with moderately strong OH···O bonds with participation of DMSO. The most intensive bands are disposed in the regions 1700–1200 and 1000–700 cm^{-1}. All these bands are essentially broadened. In some cases, the broadening is very strong, that implies the participation of the bridging proton in several corresponding vibrations. However, it is difficult to distinguish a band which should be assigned as νOH, based on the phenomenological description of the spectrum. One can also mark the absence of characteristic νS=O band in the usual region 1100–1000 cm^{-1}.

The results of quantum mechanical treatment allow one to understand these features. The most important feature of vibrational spectrum of homoconjugated bis-dimethylsulfoxide cation, established by calculations, is the involvement of proton stretching and bending coordinates in different normal modes, which results in mixing of proton vibrations with vibrations of sulfoxide moiety — νSO, νCS, δCH. This effect is greatly expressed in calculated spectrum

Table 3
Vibrational frequencies (cm^{-1}) and intensities (in brackets, km mol^{-1}) of bis-dimethylsulfoxide cation in 2000–400 cm^{-1} region

$[Me_2SO]_2H^+Cl^-$ (calc.)	$[Me_2SO]_2H^+BF_4^-$ (calc.)	Assignment	$[(Me_2SO)_2H]_2PtCl_6$ (KBr pellet)
442 (164)	465 (261)	SOHOS deform	467 (m)
651 (38)	667 (0.4)	CSC stretch	~ 670 (vw)
656 (2)	672 (17)	CSC stretch	~ 680 (vw)
694 (12)	702 (11)	CSC stretch	718 (w)
696 (10)	709 (14)	CSC stretch	735 w
882 (499)	874 (972)	νSO, OHO deform	846 (v st, br.)
922 (11)	926 (4)	CH_3 rock	?
929 (71)	937 (94)	CH_3 rock, OHO deform	?
932 (55)	947 (25)	CH_3 rock	?
959 (98)	967 (35)	CH_3 rock, OHO deform	941 (m)
966 (58)	970 (45)	CH_3 rock	~ 960 sh
995 (70)	998 (87)	CH_3 rock, OHO deform	1001 (m)
1024 (54)	1033 (46)	CH_3 rock	
1053 (118)	1070 (132)	CH_3 rock, δOH	1029 (m)
1048 (37)		δOH, CH_3 rock	
1058 (25)	1057 (39)	CH_3 rock	
	1104 (390)	δOH, H···B stretch, CH_3 rock	
	1172 (75)	δOH	
	1214 (354)	δOH, H···B stretch	
1334 (10)	1345 (6)	δCH_3	
1339 (5)	1361 (1.5)	δCH_3	1317 (w)
1362 (1)	1369 (0.9)	δCH_3	
1365 (6)	1394 (0.75)	δCH_3	1331 (w)
1441 (50)		δCH_3, δOH	
1444 (164)		δCH_3, δOH	
1452 (435)	1441 (712)	δOH, δCH_3	~ 1360–1370 (st, br)
	1452 (25)	δCH_3, δOH	
1464 (10)	1454 (13)	δCH_3	
1466 (9)		δCH_3	
1467 (9)	1466 (2)	δCH_3	
1477 (2)	1468 (5)	δCH_3	
1479 (9)	1478 (2)	δCH_3	~ 1406 (m)
1494 (6)	1499 (19)	δCH_3	
1496 (29)	1507 (24)	δCH_3	
1907 (4100)	1667 (4850)	νOH	~ 1650 (st, br)

of isolated $[(DMSO)_2H]^+$, where O···H···O bond is exactly symmetrical and proton vibrational displacements along and across hydrogen bridge are mixed with each other and with displacements of other atoms of both DMSO molecules. No pure νO···H···O mode exists in this case. Similar peculiarities of vibrational spectra were described in Ref. [13] for homoconjugated ions $H_5O_2^+$, $(CH_3O)_2H^-$ and $(CH_3OH)_2H^+$.

The mixing of vibrations is not so strong in the complexes with a counterion. In this case one can speak about the existence of characteristic νOH stretching vibration (1907 cm^{-1} in the complex with Cl^- and 1667 cm^{-1} with BF_4^-).

According to calculations, the most intensive (almost 6000 km mol^{-1}) band in spectrum of isolated homoconjugated cation belongs to vibration with frequency 710 cm^{-1}, which can be assigned as mixed νS=O and δOHO vibration. In complexes with anions the frequency of this vibration increases: to 882 cm^{-1} in the case of Cl^- and 874 cm^{-1} in the case of BF_4^- (Table 3). It is natural to expect that for $PtCl_6^-$ it should be somewhat less than for BF_4^-. Indeed, one can see in the experimental spectrum, a very strong and broadened band near 846 cm^{-1}. Another characteristic band in the spectrum of $[(DMSO)_2H]_2[PtCl_6]$ is the band at 467 cm^{-1}

(465 cm^{-1} in complex with BF_4^- and 442 cm^{-1} in complex with Cl^- with essential contribution of deformation of SOHOS fragment). These comparisons show that the calculated frequencies and forms of vibrations are rather close to the real ones. The best agreement with spectrum of the platinum salt is shown by calculated spectrum of BF_4^- complex.

The assignment of all the experimental bands observed in the higher frequency region is difficult because of their strong overlapping. However, the groups of intensive bands in the regions 850–1050 and 1300–1500 cm^{-1} can be assigned roughly as belonging to rocking and bending vibrations of CH_3 groups with significant contribution of different deformations of OHO angle. It seems that a strong broad absorption with a maximum near ~1370 cm^{-1} in the experimental spectrum is caused mainly by vibration having the most significant contribution of δOH and corresponding to vibration with a frequency of about 1440–1450 cm^{-1} in the calculated spectra. The broad band near 1650 cm^{-1} can be interpreted probably as νOH in accordance with calculated value for $[(DMSO)_2H]^+BF_4$ complex. More complete and detailed assignment studies of deuterated samples are necessary.

4. It has been found that the sample of solid $[(DMSO)_2H]_2[PtCl_6]$ salt reveals slow, but essential changes with time, which can be detected spectroscopically. Curves 2 and 3 in Fig. 2 illustrate these changes. Earlier, similar changes were found to occur with other related compounds upon heating till 100°C[14]. A remarkable feature of these changes is the appearance of a strong sharp band near 1180 cm^{-1}, that is higher than νSO frequency of free DMSO and typical for DMSO molecule coordinated via sulfur atom (curve 3). One can notice also that in this case positions and intensities of some bands belonging to vibrations of DMSO moiety, become closer to those predicted by DFT calculations for isolated monocation. Particularly, essential relative increase of intensity of the band belonging to mixed SO stretching and OHO bending vibration is observed; the maximum of the band shifts to lower frequencies (~750 cm^{-1}). It has been suggested that one of DMSO molecules bonded with bridging proton turns from the outer to the inner sphere and becomes coordinated to the metal. This can be described by reaction:

$$[(Me_2SO)_2H]_2PtCl_6 \rightarrow [Me_2SOH]^+[Me_2SOPtCl_5]^- + 2Me_2SO + HCl$$

It is seen that the product of this reaction instead of homoconjugated cation contains monocation $DMSOH^+$ hydrogen bonded with DMSO molecule coordinated to platinum. Probably, one can consider such a system as a kind of heteroconjugated cation $[Me_2SO\cdots H\cdots OMe_2SPt]^+$.

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References

[1] D. Hadzi, J. Chem. Soc. (1962) 5128.

[2] D. Hadzi, N. Kobilarov, J. Chem. Soc. A (1966) 489.

[3] A.J. Barnes, M.P. Wright, J. Chem. Soc. Faraday Trans. II 82 (1986) 165.

[4] A.J. Barnes, L. Schriver, A. Schriver, J.P. Perchard, J. Mol. Struct. 240 (1990) 239.

[5] J.M. Williams, M. Kreevoy, J. Am. Chem. Soc. 89 (1967) 5499.

[6] A.P. Kirilova, V.D. Mayorov, A.I. Serebryanskaya, N.B. Librovich, E.N. Guriyanova, Izvest. Akad. Nauk USSR, Ser. Khim. 10 (1986) 2435.

[7] R.A. Potts, Inorg. Chem. 9 (1970) 1284.

[8] B.R. James, R.H. Morris, J. Chem. Soc. Chem. Commun. (1980) 31.

[9] O.V. Rudnitskaja, T.M. Buslaeva, N.I. Lyalina, Zh. Neorg. Khim. 39 (1994) 922.

[10] V.I. Lobadyuk, V.N. Spevak, N.K. Skvortsov, A.I. Stash, V.K. Belskij, Zh. Obshch. Khim. 66 (1996) 705.

[11] M.J. Frisch, G.W. Trucs, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A.Al.-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen. M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.

[12] V.K. Belskij, private communication.

[13] G.V. Yukhnevich, E.G. Tarakanova, V.D. Mayorov, N.B. Librovich, J. Mol. Struct. 265 (1992) 237.

[14] V.I. Lobadyuk, V.N. Spevak, N.K. Skvortsov, V.M. Schreiber, Rhodium Express 17 (1996) 10.