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Description of Molecular Distortions: IV. Relationships Between the Distortion and the Hydrogen Bond Strength for Some Compounds Containing HSO₄ Ions

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Several methods are known for describing the distortions of tetrahedral molecules. In the present paper, some correlations between the hydrogen bond strength and the different measures for the distortions of HSO_4^- ions are evaluated. In terms of the distortion indices the rasults reflect similar trends to those calculated for phosphates[1]. It is found that weaker hydrogen bonding is accompanied by larger distortions of the HSO_4 tetrahedra.

INTRODUCTION

Previous works have shown that hydrogen bonding has a remarkable role in modifying the oxo-anions geometry in the HXO_4 and H_2XO_4 groups to which the hydrogen atom is attached [1-3]. Thus, the existence of correlations between the three distortion indices[4] and the hydrogen bond lenght[1] for some hydrogenphosphates, as well as correlations between X-O(H) and O-H ... O distances (in which X = B,C,N,S,Si,As,Se,I)[2,3] for a number of hydrogentetraoxoanions, were revealed. The distortions of polyatomic molecules (or ions) in the solid state, however, may be described in a varitey of ways[4-10] each method having some advantages and some shortcomings. It is therefore of interest to study the effect of hydrogen bonding in some hydrogensulfates, especially on the distortion indices[4], displacement vectors[6] and the total distortion[9] of these ions.

DEFINITIONS AND CALCULATIONS

All quantities were defined in the original papers[4,6,9].

A total of 39 hydrogensulfate ions from 30 different crystal structures[11-40] have been investigated. Data for $Ba(HSO_4)_2$ were not included in the regression analysis because the hydrogen bonds in this compound are exceptionally weak (Table I). Inaccurate structures (estimated standard deviation of bond-lengths > 1 pm) were also excluded. Compounds with proton-disorder were

TABLE I

Distortions and hydrogen bond streghts for some hydrogensulfates (data marked with* were not included in the regression analysis)

Compound	DI(TO)	DI(OTO)	DI(OC	$|D_2|/°$	$|D_3|/pm$	$|D_4|/°$	Dt	$R(O...O)/pm$	Ref.
KHSO$_4$'	0.0292	0.0310	0.0056	1.74	10.90	8.16	0.06410	261.9	[11]
KHSO$_4$'	0.0235	0.0348	0.0066	2.46	10.17	8.32	0.05973	263.0	[12]
KHSO$_4$''	0.0313	0.0304	0.0039	1.57	10.16	9.92	0.06378	257.3	[11]
KHSO$_4$''	0.0298	0.0354	0.0065	1.74	10.51	10.20	0.06756	258.3	[12]
C$_5$H$_6$N$_5$HSO$_4$	0.0256	0.0309	0.0064	1.99	8.77	8.57	0.05019	256.5	[13]
C$_{12}$H$_3$N$_2$H$_2$SO$_4$	0.0313	0.0314	0.0074	2.90	10.69	8.87	0.06407	259.4	[14]
[Co$_2$(NH$_3$)$_{10}$O$_2$]HSO$_4$)$_3$SO$_4$	0.0311	0.0284	0.0058	2.20	10.82	7.81	0.06161	255.0	[15]
[Co$_2$(NH$_3$)$_{10}$O$_2$](HSO$_4$)$_3$SO$_4$	0.0328	0.0338	0.0046	1.68	11.57	9.69	0.07350	260.0	[15]
Rb$_3$H(SO$_4$)$_2$	0.0199	0.0250	0.0035	0.28	6.86	6.72	0.03268	248.5	[16]
Pt(NH$_3$)$_4$PtBr$_2$(NH$_3$)$_4$(HSO$_4$)$_4$	0.0287	0.0277	0.0075	3.34	10.15	8.07	0.05951	258.2	[17]
NaHSO$_4$·H$_2$O	0.0409	0.0318	0.0121	4.09	14.54	9.81	0.09529	270.0	[18]
NaHSO$_4$·H$_2$O	0.0372	0.0266	0.0123	4.21	12.83	7.37	0.07420	265.8	[19]
Na$_3$H(SO$_4$)$_2$	0.0160	0.0158	0.0041	1.78	5.62	4.35	0.02103	243.2	[20]
Na$_3$H(SO$_4$)$_2$	0.0168	0.0155	0.0041	1.44	5.91	4.35	0.02240	243.4	[21]
H$_2$SO$_4$	0.0374	0.0355	0.0123	5.52	11.06	10.28	0.07481	263.0	[22]
CH$_3$C(OH)$_2$HSO$_4$	0.0261	0.0313	0.0036	0.52	8.93	8.44	0.05098	256.7	[23]
NaHSO$_4$'-α	0.0158	0.0125	0.0045	1.87	4.81	3.98	0.01695	249.7	[24]
NaHSO$_4$''-α	0.0355	0.0329	0.0073	2.73	12.24	8.94	0.07607	269.0	[24]
CsHSO$_4$	0.0251	0.0217	0.0083	2.91	7.53	7.81	0.04008	257.2	[25]
(ND$_4$)$_3$D(SO$_4$)$_2$	0.0179	0.0185	0.0001	0.27	6.09	4.97	0.02454	255.9	[26]
(ND$_4$)$_3$D(SO$_4$)'-III	0.0216	0.0217	0.0033	1.40	7.84	6.02	0.03848	254.4	[27]
(ND$_4$)$_3$D(SO$_4$)$_2$''-III	0.0191	0.0255	0.0050	1.34	7.05	7.09	0.03527	253.6	[27]
(NH$_4$)$_3$H(SO$_4$)$_2$	0.0179	0.0183	0.0012	0.12	6.10	4.94	0.02444	254.1	[28]
(NH$_4$)$_3$H(SO$_4$)$_2$	0.0170	0.0180	0.0015	0.83	5.77	4.84	0.02269	254.0	[29]
[C$_{21}$H$_{25}$N$_2$O]HSO$_4$·(1/2)H$_2$O	0.0219	0.0131	0.0093	0.80	6.57	3.99	0.02538	261.4	[30]
[Ag(C$_3$H·$_6$N·$_{10}$)]SO$_4$HSO$_4$·H$_2$O	0.0283	0.0312	0.0061	2.59	9.76	8.35	0.05704	251.0	[31]
H$_2$SO$_4$·H$_2$O	0.0284	0.0258	0.0096	3.08	9.87	7.61	0.05471	265.7	[32]
NH$_4$HSO$_4$'	0.0298	0.0344	0.0125	5.28	10.16	10.05	0.06548	251.4	[33]
NH$_4$HSO$_4$''	0.0286	0.0306	0.0054	1.78	9.81	8.63	0.05709	259.8	[34]
[CoCl$_2$(NH$_3$)$_4$HSO$_4$	0.0329	0.0325	0.0067	2.84	11.19	8.75	0.06794	261.7	[35]
C$_{15}$H$_{18}$ClN$_4$O$_3$SHSO$_4$	0.0235	0.0292	0.0292	2.10	8.54	8.71	0.04880	265.9	[36]
Mg(HSO$_4$)$_2$'	0.0273	0.0266	0.0076	2.26	9.34	7.87	0.05069	276.8	[37]
Ca(HSO$_4$)$_2$'	0.0224	0.0271	0.0122	3.84	8.06	8.30	0.04304	262.0	[38]
Ca(HSO$_4$)$_2$''	0.0300	0.0336	0.0081	3.71	10.65	9.31	0.06690	252.2	[38]
RbHSO$_4$'	0.0304	0.0305	0.0117	4.80	10.08	10.09	0.06669	253.0	[39]
RbHSO$_4$''	0.0361	0.0381	0.0057	2.27	12.49	10.31	0.08360	262.0	[39]
Ba(HSO$_4$)$_2$'*	0.0297	0.0260	0.0099	1.66	10.31	7.41	0.05629	283.0	[40]
Ba(HSO$_4$)$_2$''*	0.0309	0.0339	0.0121	4.82	10.52	9.49	0.06972	281.6	[40]

also excluded, unless the proton was disordered between the proton-donor and the proton-acceptor. H_2SO_4 was considered as the only known example of a dihydrogensulfate compound.

Calculations of the distortion indices (DI(TO), DI(OTO) and DI(OO)), displacement vetors ($D_2(E)$, $D_3(F_2)$ and $D_4(F_2)$), the total distortion (D_t) and the regression analyses were performed on a Commodore 128 micro-computer with a suitable programs written in Basic. The input data were the unit-cell parameters and the fractional coordinates of the five atoms (S, O_1, O_2, O_3, O_4). The bondlengths were not corrected for thermal motion.

RESULTS AND DISCUSSION

The distortions and the hydrogen-bond strenghts for the investigated compounds are presented in Table I, and the least-squares-best-fit lines are given in Table II. Somewhat surprisingly, the r value for the correlation between DI(OTO) and $R(O\ldots O)$ is somewhat lower than the r value for the DI(OO)-$R(O\ldots O)$ correlation. It is expected that DI(OO) should be the most »independent« distortion index, since it has been shown that the distortion of tetrahedral oxo-anions may be visualized as »a central atom moving in a rigid framework of oxygens«[4,41] Whit respect to this, the results for hydrogensulfates clearly differ from those obtained for hydrogenphosphates[1].

TABLE II

Regression relationships for the distortion indices referred to in the text

Hydrogen Sulfate Distortion Indices	Least-squares-best-fit Regression Formula	r
DI(TO)	$6.02 \times 10^{-4} \times R(O\cdots O)$/pm - 0.1285	0.63
DI(OTO)	$4.22 \times 10^{-4} \times R(O\cdots O)$/pm - 0.0816	0.44
DI(OO)	$2.20 \times 10^{-4} \times R(O\cdots O)$/pm - 0.0502	0.46
$\|D_2(E)\|/^\circ$	$0.0655 \times R(O\cdots O)$/pm - 14.64	0.33
$\|D_3(F_2)\|$/pm	$0.209 \times R(O\ldots O)$/pm - 44.79	0.63
$\|D_4(F_2)\|/^\circ$	$0.127 \times R(O\ldots O)$/pm - 25.00	0.46
D_t	$1.67 \times 10^{-3} \times R(O\ldots O)$/pm - 0.3792	0.59

The lowest value for r (0.33) was obtained for the regression of $^1D_2(E)$ on $R(O\ldots O)$, as expected. It has been shown by Murray-Rust et al.[5] that for distortions preserving C_3 co-kernel (or effective) symmetry, $D_2(E) = 0$, so the values for this distortion vector are expected to be much smaller than the values for $D_4(F_2)$ and this is, indeed, the case (see Table I). Once again, the highest value for r (Table II) is obtained for the regression of $\|D_3(F_2)\|$ on $R(O\ldots O)$ $D_3(F_2)$ being the vector analogy of the distortion index DI(TO). The correlation coefficient for the regression of D_t on $R(O\ldots O)$ is, also, rather high.

Despite the rigorous criteria under which the structures were taken into consideration, the scatter of the points (especially in the case of DI(OTO), DI(OO), $\|D_2(E)\|/^\circ$ and $\|D_4(F_2)\|/^\circ$ correlations) is very large (the situation with the hydrogenphosphate-correlations is quite similar). Since this scatter is not a result of inaccuracies in the crystal-structure determinations, it indicates that, although important, the hydrogen bonding is far from being the only cause for the distortions of oxo-anions in crystals. In a more sophisticated

approach, the interaction with (metal) cations must be taken into account. Moreover, the recent works of Finney and Savage[42,43] reveal the importance of the so-called non-bonded interactions in minimizing the crystal energy. Obviously, further work is needed to estimate the effect of these interactions on the distortion of polyatomic molecules and ions in crystals.

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SAŽETAK

Opis molekulskih distorzija: IV. Odnos između veličine distorzije i jakosti vodikove veze u spojevima s HSO_4^- ionima

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Procijenjene su korelacije jakosti vodikove veze s nekim mjerama za distorziju iona HSO_4. Rezultati su uspoređeni s onima za fosfate. Slabija vodikova veza obično je združena s većom distrozijom HSO_4-tetraedra.