*Acta Cryst.* (1983). A**39**, 647–650

# Rigid-Body Motion of the $S_2O_3^{2-}$ Group in Thiosulphates

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(*Received* 17 *August* 1982; *accepted* 18 *March* 1983)

## Abstract

The recently published thermal parameters of Ba, Na, Mg, Ni, and $NH_4$ thiosulphates have been analysed for the rigid-body motion of the $S_2O_3^{2-}$ group using the **TL** and **TLS** treatments. In the cases of Ba, Na and $NH_4$ the rigidity of the group has been established and justified by employing various rigidity tests. Librational corrections to bond lengths have been found to be appreciable. For the cases of Mg and Ni the rigidity has been observed, but due to high e.s.d.'s detailed analysis has not been made. Hamilton's test has shown that the **TLS** treatment is preferable to the **TL** in all cases.

## Introduction

The **TL** method of Cruickshank (1956) for the rigid-body analysis of molecular structures has been applied to various structures with success for many years. The short-coming of this method in choosing the centre of libration has been overcome by the **TLS** method of Schomaker & Trueblood (1968). The significance of the **TLS** over the **TL** method can be examined by using Hamilton's (1965) test.

The most widely adopted tests for checking the validity of the rigid-body assumption are those of Burns, Ferrier & McMullan (1967) (B), Hirshfeld (1976) (H), and Rosenfield, Trueblood & Dunitz (1978) (RTD). In the B test, the size, shape and orientation of the observed and calculated thermal ellipsoids are compared and each atom is labelled as rigid (*R*), doubtful (?) or non-rigid (*NR*) accordingly. The judgment on the validity of the rigidity is made in considering the number of these labels. The H test compares the mean-square vibration amplitudes (MSVA) of the bonded atoms along their bond direction. The RTD test is a generalization of the H test. In this test Hirshfeld's rigid-bond postulate is extended to a rigid-body postulate.

## This work

Each thiosulphate structure contains a $S_2O_3^{2-}$ group in the form of a slightly distorted tetrahedron. The covalent bonds between the central sulphur atom and the surrounding sulphur and oxygen atoms strongly suggest a rigid-body character for the group. In this work the rigidity has been examined using the B test in the **TL** and the H and RTD tests in the **TLS** calculations. The rigid-body parameters obtained by these methods are given in the tables. The significance of the **TLS** over the **TL** treatment has been tested and bond lengths have been corrected for libration.

For the **TL** and **TLS** analyses the program *TERRIG* (Armağan & Yücel, 1982) and *THMI* of K. N. Trueblood have respectively been utilized. In these calculations thermal parameters have been given unit weights.

*Notes on tables*

(*a*) Hamilton's generalized *R* factor, $R_G$, is defined as

$$R_G = [\sum (U_{calc} - U_{obs})^2 / \sum U_{obs}^2]^{1/2},$$

where $U$ is a component of the temperature factor in the form

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)].$$

The r.m.s. deviation is

$$[\langle (U_{obs} - U_{calc})^2 \rangle]^{1/2}.$$

(*b*) The numbering of atoms in bond lengths is that of the original papers. The values given are those between the central sulphur [S(1) or S(2)] and the surrounding atoms.

(*c*) In the **TL** and **TLS** calculations performed in the inertial frame, all conventions are those of the relevant papers.

(*d*) In the B test an asterisk denotes that the ellipsoid has an approximately circular section perpendicular to the rotation axis.

(*e*) In the H and RTD tests the differences in MSVA ($\Delta$'s) have been obtained by subtracting the values corresponding to the row atoms from those of the column atoms. The asterisk denotes the central atom.

0108-7673/83/050647-04$01.50

### Barium thiosulphate monohydrate $BaS_2O_3.H_2O$

There are two recent X-ray ($x$) (Aka, Armağan & Aydin Uraz, 1980) and neutron ($n$) (Manojlovic-Muir, 1975) structural investigations yielding almost identical structures with $R = 0{\cdot}065$ ($x$) and $R = 0{\cdot}034$ ($n$). The results of the rigid-body analysis for neutron and X-ray data are given in Table 1. The B test does not guarantee the rigid-body motion and the result lies in the doubtful region. The H test could be considered as being fulfilled since the maximum value of the MSVA difference ($\Delta$) is about $1{\cdot}5\sigma$. According to the RTD test the r.m.s. $\Delta$'s are $19 \times 10^{-4}$ Å$^2$ and $17 \times 10^{-4}$ Å$^2$, the r.m.s. values of the ratio $\Delta/\sigma(\Delta)$ are 1·1 and 1·2 for the bonded and non-bonded pairs respectively. It is therefore obvious that the non-bonded distances remain as rigid as the bonds. The bond-length correction for librational motion is at the $3\sigma$ level. Hamilton's $R$-factor-ratio test shows that the significance of the **TLS** over the **TL** treatment is justified at the 0·5% level for $n$, while it is more than 50% questionable for $x$. Large standard deviations of the X-ray thermal parameters cast doubts on the reliability of the rigid-body treatment. Comparison of $x$ and $n$ thermal parameters showed that $b_{22}$ ($x$) values are almost twice those of $b_{22}$ ($n$). This could possibly be attributed to an error in scale factor which has high correlation with $b_{22}$. Despite their low accuracies the X-ray rigid-body parameters nevertheless indicate the trend of the rigid-body motion of the group which was justified by the analysis on the neutron data.

### Sodium thiosulphate pentahydrate $Na_2S_2O_3.5H_2O$

The neutron and X-ray data used for the investigation are those of Lisensky & Levy (1978) and Aydin Uraz & Armağan (1977), respectively. These authors report almost the same structure refined to $R = 0{\cdot}089$ ($x$) and $R = 0{\cdot}055$ ($n$). The results of the rigid-body analysis for $n$ and $x$ are presented in Table 2.

The B test does not raise legitimate doubts about the rigidity of the group. For the H test the criterion values are within the acceptable range confirming the rigidity. The values of the r.m.s. $\Delta$ and the r.m.s. of the ratio $\Delta/\sigma(\Delta)$ are respectively $13 \times 10^{-4}$ Å$^2$, 0·59 ($x$) and $14 \times 10^{-4}$ Å$^2$, 0·63 ($n$) for the bonded pairs, $32 \times 10^{-4}$ Å$^2$, 0·70 ($x$) and $24 \times 10^{-4}$ Å$^2$, 1·68 ($n$) for the non-bonded pairs. It is therefore concluded that the group can be regarded as being rigid on both $x$ and $n$ data. The significance of the **TLS** over **TL** treatment is justified at the level better than 0·5% for both $x$ and $n$. The librational corrections to bond lengths are at the $2{\cdot}5\sigma$ level for $x$ and $3\sigma$ level for $n$. It is seen from Table 2 that the r.m.s. amplitudes of $n$ and $x$ are in good agreement.

Table 1. *Barium thiosulphate monohydrate* ($n$), ($x$)

E.s.d.'s are given in parentheses.

**TL** calculations

R.m.s. amplitudes

| | | | | |
|---|---|---|---|---|
| $L$ (°) | ($n$) | 5·15 | 3·80 | 3·17 |
| | ($x$) | 6·35 | 5·07 | 2·90 |
| $T$ (Å) | ($n$) | 0·113 | 0·098 | 0·093 |
| | ($x$) | 0·148 | 0·138 | 0·084 |

R.m.s. deviations (Å$^2$)

($n$) 0·0016 ($x$) 0·0058

**TLS** calculations

**L** (°$^2$) ($n$)

| | | |
|---|---|---|
| 26·0 (2·6) | 0·9 (2·3) | 4·7 (2·3) |
| | 13·3 (3·0) | −0·3 (1·5) |
| | | 10·9 (3·0) |

**T** ($10^{-3}$ Å$^2$)

| | | |
|---|---|---|
| 11·1 (0·7) | 1·8 (0·7) | 1·3 (0·7) |
| | 10·4 (0·9) | −1·5 (0·6) |
| | | 10·2 (0·9) |

**S** (Å °)

| | | |
|---|---|---|
| 0·05 (3) | −0·10 (3) | −0·05 (3) |
| −0·03 (2) | 0·03 (3) | 0·03 (2) |
| −0·03 (2) | 0·01 (1) | −0·08 (3) |

R.m.s. amplitudes

| | | | | |
|---|---|---|---|---|
| $L$ (°) | ($n$) | 5·24 | 3·65 | 3·08 |
| | ($x$) | 6·58 | 4·88 | 1·96 |
| $T$ (Å) | ($n$) | 0·117 | 0·097 | 0·093 |
| | ($x$) | 0·146 | 0·130 | 0·105 |

B test ($n$)

| | $U^o - U^c$ | $\sigma$ | $S$ | $\theta$ | | |
|---|---|---|---|---|---|---|
| S(1) | −21 | 33 | 178 | 38* | ? | ($\bar{3}12$) |
| S(2) | −5 | 35 | 624 | 26 | *NR* | ($2\bar{3}1$) |
| O(1) | 16 | 20 | 50 | 13 | *R* | |
| O(2) | 14 | 17 | 68 | 42 | *NR* | ($\bar{3}2\bar{1}$) |
| O(3) | −3 | 18 | 45 | 18 | *R* | |

$R_G$

($n$) 0·134 ($x$) 0·280

H and RTD tests $\Delta(10^{-4}$ Å$^2)$ ($n$)

| | S(1) | S(2) | O(1) | O(2) | O(3) |
|---|---|---|---|---|---|
| S(1)* | 0 | 8 (22) | 4 (21) | 28 (19) | 23 (15) |
| S(2) | | 0 | 25 (20) | 33 (13) | 7 (22) |
| O(1) | | | 0 | 3 (16) | 7 (9) |
| O(2) | | | | 0 | 1 (9) |
| O(3) | | | | | 0 |

Bond lengths (Å) ($n$)

| | Uncorrected | Corrected |
|---|---|---|
| S(1)–S(2) | 1·979 (3) | 1·987 |
| S(1)–O(1) | 1·483 (3) | 1·493 |
| S(1)–O(2) | 1·472 (3) | 1·482 |
| S(1)–O(3) | 1·475 (3) | 1·483 |

$R_G$

($n$) 0·056 ($x$) 0·243

R.m.s. deviation (Å$^2$)

($n$) 0·0007 ($x$) 0·0050

* See notes on tables.

Table 2. *Sodium thiosulphate pentahydrate* (*n*), (*x*)

E.s.d.'s are given in parentheses.

**TL** calculations
R.m.s. amplitudes

| | | | | |
|---|---|---|---|---|
| *L* (°) | (*n*) | 5·95 | 5·13 | 2·09 |
| | (*x*) | 5·44 | 5·04 | 2·69 |
| *T* (Å) | (*n*) | 0·149 | 0·132 | 0·110 |
| | (*x*) | 0·140 | 0·123 | 0·092 |

R.m.s. deviation (Å²)

(*n*) 0·0024 (*x*) 0·0026

**TLS** calculations
**L** (°²) (*n*)

| | | |
|---|---|---|
| 27·4 (3·1) | 3·4 (3·1) | 2·5 (3·8) |
| | 20·9 (2·0) | 6·4 (3·3) |
| | | 17·1 (2·6) |

**T** ($10^{-3}$ Å²)

| | | |
|---|---|---|
| 20·5 (0·8) | −1·4 (0·8) | 0·2 (1·0) |
| | 14·4 (0·6) | 2·3 (0·9) |
| | | 15·2 (1·1) |

**S** (Å °)

| | | |
|---|---|---|
| −0·06 (4) | −0·09 (4) | −0·09 (3) |
| −0·07 (3) | −0·01 (4) | 0·03 (4) |
| 0·05 (4) | −0·13 (3) | 0·07 (2) |

R.m.s. amplitudes

| | | | | |
|---|---|---|---|---|
| *L* (°) | (*n*) | 5·55 | 4·72 | 3·51 |
| | (*x*) | 5·37 | 4·54 | 3·64 |
| *T* (Å) | (*n*) | 0·145 | 0·130 | 0·111 |
| | (*x*) | 0·138 | 0·118 | 0·094 |

B test (*n*)

| | $U^o - U^c$ | $\sigma$ | *S* | $\theta$ | | |
|---|---|---|---|---|---|---|
| S(1) | −101 | 36 | 3 | 30 | ? | |
| S(2) | −2 | 33 | 14 | 28* | *R* | (3$\bar{2}$1) |
| O(1) | 71 | 22 | 37 | 45 | *NR* | (3$\bar{2}$1) |
| O(2) | 61 | 22 | 9 | 20 | ? | |
| O(3) | −29 | 21 | 27 | 24 | *R* | (3$\bar{2}$1) |

$R_G$

(*n*) 0·120 (*x*) 0·150

H and RTD tests $\Delta(10^{-4}$ Å²) (*n*)

| | S(1) | S(2) | O(1) | O(2) | O(3) |
|---|---|---|---|---|---|
| S(1) | 0 | 12 (22) | 40 (16) | 43 (17) | 12 (7) |
| S(2)* | | 0 | 18 (20) | 15 (30) | −9 (18) |
| O(1) | | | 0 | 20 (19) | 8 (17) |
| O(2) | | | | 0 | 4 (15) |
| O(3) | | | | | 0 |

Bond lengths (Å) (*n*)

| | Uncorrected | Corrected |
|---|---|---|
| S(2)–S(1) | 2·020 (4) | 2·031 |
| S(2)–O(1) | 1·454 (3) | 1·465 |
| S(2)–O(2) | 1·458 (3) | 1·468 |
| S(2)–O(3) | 1·477 (3) | 1·487 |

$R_G$

(*n*) 0·036 (*x*) 0·057

R.m.s. deviation (Å²)

(*n*) 0·0007 (*x*) 0·0010

* See notes on tables.

Table 3. *Magnesium and nickel thiosulphate hexahydrate* (*first and second lines, respectively*)

E.s.d.'s are given in parentheses.

| **TL** (R.m.s. amplitudes) | | | | | | **TLS** | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *L* (°) | | | *T* (Å) | | | *L* (°) | | | *T* (Å) | | |
| 4·75 | 3·72 | 1·78 | 0·177 | 0·128 | 0·116 | 4·68 | 4·39 | 0·79 | 0·170 | 0·123 | 0·109 |
| 8·15 | 4·90 | imag. | 0·153 | 0·107 | 0·100 | 6·52 | 5·02 | 2·73 | 0·152 | 0·125 | 0·059 |
| | $R_G$ | | R.m.s. deviation (Å²) | | | | $R_G$ | | R.m.s. deviation (Å²) | | |
| | 0·232 | | 0·0048 | | | | 0·153 | | 0·0031 | | |
| | 0·206 | | 0·0046 | | | | 0·130 | | 0·0027 | | |

### Magnesium thiosulphate hexahydrate and nickel thiosulphate hexahydrate ($MgS_2O_3.6H_2O$, $NiS_2O_3.6H_2O$)

The thermal data used for magnesium (MT) and nickel thiosulphates (NT) are those of Baggio, Amzel & Becka (1969) and Elerman, Aydin Uraz & Armağan (1978), respectively. Using the X-ray data the structures of MT and NT have been refined by the authors to $R = 0{\cdot}085$ and $R = 0{\cdot}056$. The rigid-body analysis indicated the rigidity of the group. The high e.s.d.'s of the rigid-body parameters reflected the poor quality of the data. Hence, only certain indicative parameters are given in Table 3. The **TLS** is significant at the 20% level over the **TL** treatment. The most recent study performed on the highly accurate data of MT yielded unequivocally the rigid character of the group (Elerman, 1982).

### Ammonium thiosulphate $(NH_4)_2S_2O_3$

The analysis was made using the X-ray data of Teng, Fuess & Bats (1979). The structure has been refined to $R = 0{\cdot}032$. The results of the rigid-body analysis are presented in Table 4. Both **TL** and **TLS** analyses reveal the rigidity which is also confirmed by the B test. In the B test only one atom has an unacceptable size parameter, namely $3{\cdot}7\sigma$, obviously not bad enough to justify the group as non-rigid. The H test also establishes the rigidity with acceptable criterion values. As for the RTD test the values of the r.m.s. $\Delta$

Table 4. *Ammonium thiosulphate*

**TL** calculations

R.m.s. amplitudes

| | | | |
|---|---|---|---|
| $L$ (°) | 8·56 | 5·68 | 2·82 |
| $T$ (Å) | 0·173 | 0·149 | 0·130 |

| $R_G$ | R.m.s. deviation |
|---|---|
| 0·122 | 0·0036 (Å²) |

**TLS** calculations

**L** (°²)

| | | |
|---|---|---|
| 54·8 (3·0) | 15·6 (3·0) | −8·1 (3·5) |
| | 28·3 (3·0) | −1·9 (2·9) |
| | | 31·7 (3·2) |

**T** ($10^{-3}$ Å²)

| | | |
|---|---|---|
| 23·2 (0·8) | 3·2 (0·8) | −1·0 (0·9) |
| | 22·2 (0·8) | −2·0 (0·9) |
| | | 23·3 (0·9) |

**S** (Å °)

| | | |
|---|---|---|
| 0·20 (3) | −0·13 (4) | −0·18 (4) |
| 0·20 (3) | −0·11 (4) | −0·02 (2) |
| −0·06 (3) | −0·01 (3) | −0·09 (3) |

R.m.s. amplitudes

| | | | |
|---|---|---|---|
| $L$ (°) | 8·00 | 5·48 | 4·55 |
| $T$ (Å) | 0·165 | 0·150 | 0·139 |

B test

| | $U^o - U^c$ | $\sigma$ | $S$ | $\theta$ | | |
|---|---|---|---|---|---|---|
| S(1) | −17 | 14 | 24 | 20 | $R$ | |
| S(2) | −8 | 9 | 108 | 25 | $R$ | $(\bar{3}2\bar{1})$ |
| O(1) | −109 | 29 | 53 | 23 | $NR$ | |
| O(2) | 56 | 40 | 2 | 5 | $R$ | $(32\bar{1})$ |
| O(3) | 78 | 50 | 28 | 15 | $R$ | |

H and RTD tests $\Delta$ ($10^{-4}$ Å²)

| | S(1) | S(2) | O(1) | O(2) | O(3) |
|---|---|---|---|---|---|
| S(1) | 0 | 15 (7) | 24 (17) | 1 (12) | 17 (24) |
| S(2)* | | 0 | 9 (22) | 12 (9) | 8 (18) |
| O(1) | | | 0 | 31 (25) | 24 (38) |
| O(2) | | | | 0 | 16 (24) |
| O(3) | | | | | 0 |

Bond lengths (Å)

| | Uncorrected | Corrected |
|---|---|---|
| S(2)–S(1) | 1·979 (1) | 1·997 |
| S(2)–O(1) | 1·476 (2) | 1·492 |
| S(2)–O(2) | 1·472 (3) | 1·488 |
| S(2)–O(3) | 1·465 (2) | 1·487 |

| $R_G$ | R.m.s. deviation (Å²) |
|---|---|
| 0·022 | 0·0007 |

* See notes on tables.

and r.m.s. $\Delta/\sigma(\Delta)$ are $11 \times 10^{-4}$ Å², 0·77 for the bonded and $21 \times 10^{-4}$ Å², 0·90 for the non-bonded pairs. Hence it also confirms the rigidity. The **TLS** is significant over the **TL** treatment at a level much lower than 0·5%. The librational corrections are well beyond the quoted bond-length e.s.d.'s.

## Conclusions

The investigation of the seven sets of data revealed that the thermal motion of the $S_2O_3^{2-}$ group can be described by the rigid-body motion hypothesis without ambiguity. The large e.s.d.'s observed arise from the poor quality of the data, not from the non-rigid character of the group.

The use of the **TLS** over the **TL** treatment is justified and the B, H and RTD rigidity tests are fulfilled. Librational corrections to the bond lengths are found to be significant.

The inertial axis, which has the smallest moment of inertia of the $S_2O_3^{2-}$ group and coincides with the S(1)–S(2) bond direction, lies close to the largest libration axis. The r.m.s. librational amplitudes increase as the moments of inertia for the relevant axes decrease. For the thiosulphates examined the variation observed in the r.m.s. values of the librational and translational amplitudes and in the orientation of the principal axes with respect to the inertial axes could be attributed to the environmental interactions which may restrict the motions of the rigid group but not affect its rigidity.

It appears evident that in order to obtain rigid-body parameters to make sound physical interpretation one has to collect accurate intensity data free as much as possible from random and systematic errors and to use appropriate structural modes.

The author is indebted to Dr A. Yüçel for his appreciable help and thanks E. Yücel and İ. Ünver of the Turkish Ministry of Commerce for their support in the computations.

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