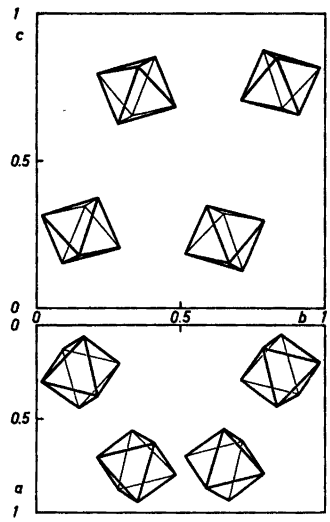

Fig. 1. Projection of the positions of Bi-atoms in one unit cell of $Bi_6(OH)_{12}(ClO_4)_6$ on the *bc*-plane (upper part) and on the *ab*-plane (lower part).

range from 3.64(1) to 3.77(1) Å along the edges, and from 5.18(1) to 5.22(1) Å along the diagonals. The shortest Bi – Bi distance between two different octahedra is 8.78(2) Å, clearly showing that the crystal contains discrete hexanuclear bismuth complexes. The Bi – Bi distances found are close to the corresponding distance of 3.70 Å deduced by Levy *et al.* for the complexes in solution.

A complete structure determination is in progress.

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Structure of Gaseous Dimethyltrithiocarbonate Studied by Electron Diffraction

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Methyl vinyl sulfide has been shown by electron-diffraction [1,2] and by vibrational spectroscopy [3,4] to exist in two conformers, one *syn* (or *cis*) form and a *gauche* form with a non-planar skeleton. The infrared and Raman spectra of liquid and cryst. dimethyltrithiocarbonate, $S=C(SCH_3)_2$, have been reported [5,6] and the presence of two conformers was found in the liquid state. As a part of a study of the conformational properties of molecules with $C(sp^2)-S$ bonds, we have investigated dimethyltrithiocarbonate by means of electron-diffraction measurements.

The electron-diffraction data were recorded with the Oslo apparatus.[7] A modified molecular intensity curve ranging from $s=1.50$ Å^{-1} to $s=41.0$ Å^{-1}, was obtained in the usual way.[8] The experimental radial distribution (RD) function obtained by Fourier inversion of the intensity curve, is shown in Fig. 1.

The most likely conformers for this molecule are the *syn-syn* form shown in Fig. 1, a *syn-anti* form which also has a planar skeleton, and non-planar forms, *e.g. syn-gauche* or *gauche-gauche*. Calculations of theoretical RD functions showed that only the *syn-syn* form was consistent with the electron-diffraction data. Least-squares refinements were therefore carried out assuming this model.

The simple force field given in Table 1, which yielded frequencies in reasonable agree-

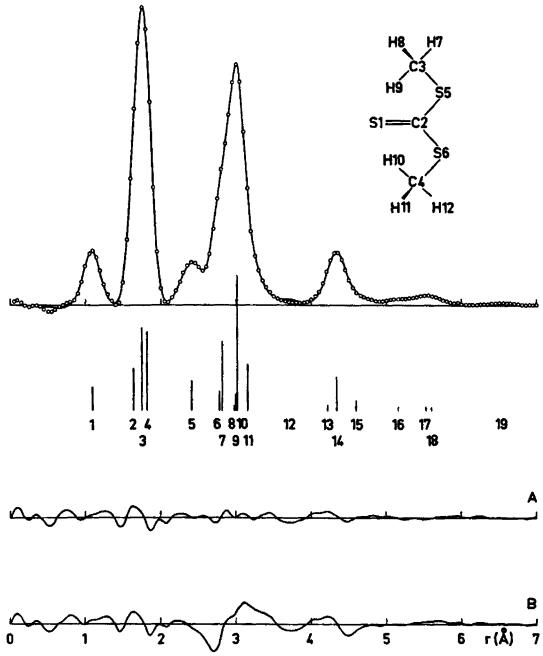

Fig. 1. Experimental (circles) and theoretical RD functions for dimethyltrithiocarbonate. Curve A shows the differences between experimental and theoretical values, and curve B the differences when the theoretical curve is calculated with 30 % of a *syn-anti* form. The scale of the difference curves is twice as large as for the RD curves. 1, C3 – H7; 2, S1 – C2; 3, S5 – C2; 4, S5 – C3; 5, S5···H7; 6, C2···C3; 7, S5···S6; 8, C2···H8; 9, S1···H8; 10, S1···S5; 11, S1···C3; 12, C2···H7; 13, S1···H7; 14, S5···C4; 15, S5···H10; 16, S5···H12; 17, C3···C4; 18, C3···H10; 19, C3···H12.

ment with the observed ones,[5,6] was used to compute mean amplitudes of vibration (u) and perpendicular amplitude correction coefficients (K) by the method described by Stølevik *et al.*[9] Some of the u values are included in Tables 2 and 3. The K values were used to obtain the R_α-structure [10] which is geometrically consistent, and in this way include the shrinkage effects [10] in the refinements.

Since the three CS bond distances contribute to the same peak in the RD curve, the determination of the individual distances is rather difficult. The corresponding mean amplitudes could not be refined independently. Two calculations were performed. In the first one the differences between the u(CS) values were assumed to be the same as computed from spectroscopic data, and one u parameter was refined. In the second calculation the u values given in Table 1 were assumed. The difference in the results was insignificant; for the CS bond lengths about 0.001 Å. We consider the structural parameters in Tables 2 and 3 as our final results.

An X-ray diffraction investigation of ethylene trithiocarbonate, $S=C\begin{smallmatrix}S-CH_2\\ \\ S-CH_2\end{smallmatrix}$, gave 1.65_2, 1.73_8, and 1.81_8 Å for the CS bonds.[11] The observed differences in the bond lengths in the two compounds may be real and related to the difference in bond angles and torsional angles. However, the comparison is somewhat uncertain because of the mentioned difficulty for dimethyltrithiocarbonate. To get a better estimate of the importance of the correlation between the distance parameters, we fixed the longest CS distance at 1.815 Å. C_2-S_5 and S=C refined then to 1.746 and 1.638 Å, respectively, while the shifts in the bond angles were insignificant. The increase in the R factor [12] was about 15 %.

The difference between the experimental RD curve and the one calculated for the pure *syn-syn* form, using the parameters from Tables 2 and 3, is given by curve A in Fig. 1. This curve shows that the experimental data can be reproduced satisfactorily by assuming the *syn-syn* form as the only conformer. The RD curves for

Table 1. Force constants used in the calculation of mean amplitudes of vibration and perpendicular amplitude correction coefficients. The number of contributions of each type is given in parentheses.

Stretching constants (mdyn Å^{-1})		Bending constants (mdyn Å rad^{-2})	
$S_1=C$	3.60(1)	$S_1C_2S_5$	0.70(2)
S_5-C_2	3.00(2)	$S_5C_2S_6$	0.70(1)
S_5-C_3	2.20(2)	$C_2S_5C_3$	1.00(2)
C–H	4.40(6)	SCH	0.35(6)
		HCH	0.45(6)
Repulsion constant (mdyn Å^{-1})		**Stretch/stretch coupling (mdyn Å^{-1})**	
$S_1\cdots S_5$	0.20(2)	$S_1=C/S_5-C_2$	0.40(2)
$C_2\cdots C_4$	0.20(2)	S_5-C_2/S_6-C_2	0.80(1)
$S_1\cdots C_4$	0.10(2)		
$S\cdots H$	0.30(6)		
$H\cdots H$	0.22(6)		
Torsional constants (mdyn Å rad^{-2})		**Out-of-plane constants [a] (mdyn Å rad^{-2})**	
$S_1C_2S_5C_3$	0.06(2)	$S_1S_5C_2/C_2S_6$	0.09(1)
$S_6C_2S_5C_3$	0.06(2)	$S_5S_6C_2/C_2S_1$	0.09(1)
$C_2S_6C_4H$	0.04(6)		

[a] C_2S_6 bond out of $S_1S_5C_2$ plane *etc.*

Table 2. Bond distances, corresponding mean amplitudes of vibration, and bond angles in dimethyltrithiocarbonate.

	r_a(Å)[a]	u(Å)[b]
S=C	1.634(5)	0.048_9
C_2-S_5	1.752(4)	0.052_5
C_3-S_5	1.800(6)	0.053_4
C–H	1.090(10)	0.078
$\angle S_1C_2S_5$	126.2(2)°	
∠CSC	103.3(4)°	
∠SCH	111.2(8)°	

[a] Results from least-squares refinement on the electron-diffraction data. The standard deviations given in parentheses apply to the last decimal place. Corrections for the correlation between the data have been included.

[b] Mean-amplitudes of vibration computed with the force field in Table 1.

Table 3. Non-bonded distances and the corresponding mean amplitudes obtained by electron diffraction (u^{ED}) and from spectroscopic data (u^{S}).

	r_a(Å)	u^{ED}(Å)	u^{S}(Å)
$S_1\cdots S_5$	3.016	0.067	0.066
$S_5\cdots S_6$	2.826	0.086	0.087
$S_1\cdots C_3$	3.156	0.125	0.127
$S_5\cdots C_4$	4.333	0.094	0.089
$C_2\cdots C_3$	2.777	–	0.083
$C_3\cdots C_4$	5.519	–	0.114
$S_5\cdots H_7$	2.401	0.113	0.115

non-planar conformers must deviate considerably from the curve corresponding to the *syn-syn* form, particularly in the region 3.0 – 4.5 Å, because of large changes in at least two C···S distances. Unfortunately the RD curves for *syn-anti* and *syn-syn* forms may be rather similar, since for example the lengths of the distances $S_1\cdots C_4$ and $S_5\cdots C_4$ may be nearly interchanged by a 180° rotation about C_2-S_6. However, the small peak near 5.5 Å found in the experimental RD curve, corresponds to the $C_3\cdots C_4$ distance in the *syn-syn* form only, proving this to be the main conformer. Curve B in Fig. 1 shows the difference between the experimental RD curve and a theoretical one calculated with 70 % of *syn-syn-* and 30 % of the *syn-anti* form. The bond distances and angles were assumed to be the same in both conformers. This difference curve is clearly not satisfactory. In spite of the possibility of better agreement by adjusting some of the bond angles in the less stable conformer, the excellent agreement for the *syn-syn* form makes it very unlikely that the amount of this conformer is less than about 75 %. A further support for this conclusion is obtained from Table 3, which shows that the mean amplitudes obtained from the electron-diffraction data for the most important non-bonded distances agree very well with those computed from the force constants in Table 1. Our result is in agreement with the observation that the *syn-syn* form is dominating in solution in non-polar solvents.[5] The large amount of *syn-syn* form in dimethyltrithiocarbonate contrasts with the results for 1,1-bis(methylthio)-ethylene where a non-planar form appears to be dominating.[13]

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Reaction Rate Studies of the Acid Hydrolysis of Some Chromium(III) Complexes. IV. Reaction Products of the Acid Hydrolysis of Pentaammineaquachromium(III)

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The authors of two recent papers [1,2] on the aquation in acid solution of the pentaammineaquachromium(III) ion disagree about the nature of the reaction products. The discrepancies between the reported results are summarized in Table 1. No quantitative error limits are given for the reaction rate constants of Ref. 2, but it is stated that the *trans*-tetraamminediaquachromium(III) ion is a significant reaction product. Contrary to this result the *trans*-tetraammine ion was not found in detectable amounts according to Ref. 1.

Table 1. Comparison between reaction rate constants at 75 °C in a 1 M perchlorate medium for formation of *cis*- (k_{5c}) and *trans*-tetraamminediaquachromium(III) (k_{5t}) from pentaammineaquachromium(III).

	$10^6 \times k_{5c}$ (s^{-1})	$10^6 \times k_{5t}$ (s^{-1})	$10^6 \times (k_{5c} + k_{5t})$ (s^{-1})
Ref. 1	83.1 ± 1.4	0.0 ± 0.8	83.1 ± 1.4
Ref. 2	~ 60	~ 15	77, 78

Different experimental approaches to the kinetic investigation were employed in the two papers. In Ref. 1, changes in the visible absorption spectra of a series of quenched reaction mixtures were directly converted into reaction rate constants. In Ref. 2, however, the overall reaction rate constant for disappearance of the pentaammine ion was obtained after separation of unreacted pentaammine ions from the quenched reaction mixtures by ion exchange chromatography in basic solution. This total reaction rate constant was then separated into *cis* and *trans* isomer contributions by analysis of the spectral characteristics, in a narrow region around the maximum of the first spin allowed absorption band, of a tetraammine mixture obtained by ion exchange chromatography in basic solution of a hydrolysed solution of pentaammineaquachromium(III) ions.

As the agreement between the overall reaction rate constant in the two papers must be considered satisfactory we have made further experiments on the behaviour of the isomeric tetraammine ions by elution on Dowex 50W X8 columns with strong sodium hydroxide solution.

As reported in Ref. 2 the molar absorption coefficient around 500 nm of the acidified tetraammine eluate obtained from hydrolysed pentaammineaquachromium(III) solutions is intermediate between those of the two pure tetraammine isomers. However, for the same solutions a molar absorption coefficient at the maximum of the second spin allowed absorption band lower than those of both tetraammine isomers was also observed. This latter observation is obviously in disagreement with formulation of the column eluate as a mixture of the isomeric tetraammines only. As resin induced complex decomposition is sometimes encountered authentic samples of the two tetraammine isomers were subjected to the sodium hydroxide elution used for the separation of the pentaammine reaction mixtures. For both isomers such resin induced decomposition was found as judged by the visible absorption spectra of acidified column eluates.

For the visible absorption spectra of both tetraammine isomers lower molar absorption