THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIS(PENTAMETHYLENEDITHIOCARBAMATE) CHROMIUM(III)-CHLOROFORM (1 : 2)

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The crystal and molecular structure of $[Cr(S_2CN(CH_2)_5)_3].2\,CHCl_3$ was found by the X-ray structural analysis method. The value R 0·090 was found for 1 131 observed independent reflections. The substance crystallizes in a space group of symmetry $P2_12_12_1$ with the following unit cell dimensions: $a = 0{\cdot}8675\,(6)$, $b = 1{\cdot}815\,(2)$, $c = 2{\cdot}155\,(3)$ nm. The experimentally observed crystal density was 1·48 Mgm^{-3} and the value calculated for $Z = 4$ was 1·51 Mgm^{-3}. The CrS_6 coordination polyhedron has the shape of a trigonally distorted octahedron, where the D_3 symmetry is approximately retained. The degree of trigonal distortion expressed as the projection of the chelate S—Cr—S angle onto the plane perpendicular to the C_3 pseudo axis is $\Phi = 41{\cdot}7°$ ($\Phi = 60°$ for an octahedron). The skeleton of the structure formed by the complex molecules contains channels filled with chloroform molecules. The specific type of complex-chloroform interaction consists of the formation of hydrogen bonds of the chloroform protons with the fully occupied p_π-orbitals of the sulphur atoms in the coordination polyhedra. The low stability and crystal decomposition can be explained by loss of chloroform from the channels.

Complexes of the $[M(S_2CNR_2)_3]$ type, where R is an alkyl, aryl or methylene ring and M is a metal atom with oxidation state III, form an unusually wide range of various crystallographic and molecular forms. Although they are all monomers, the coordination geometry and location of the molecule in the crystal depend markedly on the electronic configuration of the central atom and the character of the substituent. Tris-complexes of the transition metals not subject to electronic distortion have been studied in the greatest detail. These complexes are characterized by equality of the metal-sulphur bonds and trigonal distortion of the coordination polyhedron, resulting in racemization in solution through trigonal shift[1-5]. Interest in the structural study of tris-dithiocarbamates was also aroused by the fact that their crystallization is frequently accompanied by the formation of solvates with polar and non-polar solvents (chloroform, dichloromethane, benzene), where crystals can be prepared from either the solvated or the unsolvated complex[6]. The chloroform solvates usually rapidly decompose as a result of loss of chloroform and their stability is increased only when the complexes contain cyclic N-substituents.

This work was carried out primarily in order to analyze in detail the geometry of the coordination sphere of the $[Cr(S_2CN(CH_2)_5)_3]$ complex and to determine the type of complex–chloroform interaction.

EXPERIMENTAL

Preparation of Single Crystals

The powder sample of $[Cr(S_2CN(CH_2)_5)_3]$ was recrystallized from distilled chloroform and the blue-purple rhombohedral-prismatic crystals formed gradually became dull in the air and changed to a pale blue colour. The decomposed crystals were again recrystallized from chloroform and the diffraction pattern recorded immediately after removing the crystals from the mother liquor indicated that the substance is initially perfectly crystalline. The results of elemental analysis carried out on the crystals about 10 min after removing from the mother liquor (Table I) indicated the presence of two chloroform molecules (per complex molecule) originally clathrated in the crystal structure. Elemental analysis of the decomposed crystals indicated (Table I) that the decomposition is caused by loss of chloroform. Thus the freshly prepared crystals were stored in a closed chloroform atmosphere and were prepared for yielding experimental data.

Crystallographic Data

The approximate values of the lattice parameters found from the rotation and Weissenberg pattern were refined on a Syntex $P2_1$ diffractometer by the least squares method on the basis

TABLE I

a Results of the Elemental Analysis of the $[Cr(S_2CN(CH_2)_5)_3]$ Complex Measured Approx. 10 min after Removing the Crystals from a Chloroform Solution (calculated for $[Cr(S_2CN.(CH_2)_5)_3]2\ CHCl_3$, M.W. 771·5)

Element	S	C	N	H	Cl
% found	25·42	31·80	5·56	4·36	25·74
% calc.	24·93	31·13	5·45	4·18	27·57

b The Results of Elemental Analysis of Decomposed Crystals of $[Cr(S_2CN(CH_2)_5)_3]$ (calculated for $[Cr(S_2CN(CH_2)_5)_3]$, M.W. = 532·8)

Element	S	C	N	H	Cl
% found	35·55	40·21	7·51	5·69	2·11
% calc.	36·10	40·57	7·89	5·67	—

of 8 precisely centered reflections (MoK_α radiation): $a = 0{\cdot}8675\ (6)$, $b = 1{\cdot}815\ (2)$, $c = 2{\cdot}155\ (3)$ nm, $V = 3{\cdot}3935\ nm^3$. The crystal density $D_0 = 1{\cdot}48\ Mgm^{-3}$ measured in a bromoform–ethanol mixture is in good agreement with the calculated value $D_c = 1{\cdot}51\ Mgm^{-3}$ assuming 4 formula units per unit cell (one formula unit = $[Cr(S_2CN(CH_2)_5)_3.2\ CHCl_3]$). The linear absorption coefficient $\mu(MoK_\alpha) = 11{\cdot}9\ cm^{-1}$.

Preliminary Weissenberg patterns indicated marked broadening of the spots of the individual reflections after about 20 h after removal of the crystals from the chloroform solution; thus it was decided to measure the intensities of two crystals as a maximum diffraction angle of $2\Theta = 38°$ using MoK_α radiation.

Both crystals used for measuring the intensities were rhombohedral prisms (most rapid growth along the *a*-axis) with well-formed faces of the $\{001\}$, $\{010\}$ and $\{011\}$ types with the following dimensions: crystal(1) $0{\cdot}1 \times 0{\cdot}15 \times 0{\cdot}25\ nm^3$, crystal(2) $0{\cdot}15 \times 0{\cdot}20 \times 0{\cdot}50\ mm^3$.

Solution and Refining of the Crystal Structure

The integral intensities of the two crystals were measured on a four-cycle computer-controlled Syntex $P2_1$ diffractometer using graphite monochromated MoK_α radiation and the scanning technique $\Theta : 2\Theta$. To include the crystal mozaicity and peak splitting as a result of the presence of the K_{α_1} and K_{α_2} components, the scanning range was adjusted automatically in dependence on the diffraction angle and was 1° less than the calculated K_{α_1} position up to 1° above the calculated K_{α_2} position. The scanning rate was adjusted automatically on the basis of preliminary two-second measurement of the intensity. Because crystal decomposition during the measurement resulted in gradual decrease in the effective crystal volume and thus in the intensity of the individual reflections, the intensities of two control reflections were measured as a standard at the beginning and then periodically after each 96 recorded intensities. The time dependence of the intensities of the standard reflections can be expressed by the relationship $I = I_0 \exp(-kt)$, where I_0 is the integral intensity given by the standard reflection at the beginning (after removing the crystal from the mother liquor), k is approximately $5{\cdot}9 \,.\, 10^{-4}\ min^{-1}$ and t is the time in min. This relationship is roughly linear over the time required for the recording. The measured intensities were corrected for the intensity decrease using scaling factors found for each group of 96 reflections by comparing the intensity of each standard reflection with its initial value. To correct the set of intensities measure for crystal (*1*) to a common scale relative to crystal (*2*), the intensities of reflections in two sufficiently distant regions in reciprocal space (002—0.2.19) and 301—3.2.17 were recorded for both crystals. This scaling factor was averaged arithmetically on the basis of comparison with the scaling factors converting the measured intensities for the two crystals to an absolute scale using the Wilson statistical method and was used for final scaling.

The intensities of all reflections were corrected for the Lorentz and polarization factors and absorption was ignored. The overall number of recorded independent reflections was 1 512, of which 1 131 with $I \geqq 1.\ 96\sigma(I)$ were classified as "observed" and were used for the final structure solution.

The three-dimensional Patterson function calculated from the contributions of 1 131 observed reflections indicated the position of the chromium atom ($x = 0{\cdot}25$, $y = 0{\cdot}34$, $z = 0{\cdot}31$). The electron density distribution calculated from the three-dimensional Fourier synthesis phased from the contribution of the chromium atom indicated octahedral pseudosymmetry with respect to the Cr atom and the *R*-factor had a value of 0·61 ($R = \sum||F_0| - |F_c||/\sum|F_0|$). As the coordination sphere of the CrS_6 complex cannot have octahedral symmetry as a result of the small chelate angle of the dithiocarbamate ligand ($\sim 75°$), unambiguous phasing with several possible molecular configurations does not result from this distribution. Thus, also considering that the asymmetrical structural unit contains a marked number of "heavy" atoms with roughly equal atomic numbers, the structure was solved by the direct phasing method.

In the first stage the Tanfor[7] program was employed and 183 reflections with $|E_{\bar{h}}| \geqq 1{\cdot}44$ were used in the phase calculation. The origin of the coordinate system was defined by assigning values of $\pi/2$ to the phases of three-dimensional reflections (130, 055 and 034), which represent a linearly independent system mod (222). As intensity invariants cannot be formed for type φ_{u0u} and φ_{gu0} phases from these three origin-defining reflections, one of the two possible enantiomorphic structures was unambiguously specified by assignment of zero value for the φ_{166} phase. Three symbolic phases were assigned numerical values so that it was possible to form 16 independent starting sets. Further phases were generated for each of these sets using the tangent formula in 26 iteration cycles and were refined; reflections were eliminated during the refinement when the change in their phase from the previous cycle was $> 1/2\pi$. The set of phases with the lowest value $R_{\mathrm{Karle}} = 0{\cdot}26$ ($R_{\mathrm{Karlo}} = \sum||E_{\bar{h}}| - |E_{\bar{h}}|_c|/\sum|E_{\bar{h}}|$) was used to calculate the E-synthesis which confirmed and refined the position of the chromium atoms found from the Patterson synthesis and unambiguously defined the configuration of the CrS_6 coordination sphere. The synthesis also contained a large number of roughly equal peaks, where it was impossible to distinguish real from false ones. The Fourier synthesis of the approximate electron density calculated from the contribution of the CrW_6 fragments considerably reduced the number of maxima, but indicated the positions of only 5 further atoms in the vicinity of the sulphur atoms; the R factor had a value of 0·41.

At this stage in the structure solution the Karle method[8] was used, based on iterative refinement of the phases by the tangent formula using information from partially solved structures. The initial set of 150 phases was obtained by calculation from the partial structure of CrS_6, where the phases were accepted when they satisfied the following two criteria: *1*) $|F_c| \geqq p|F_0|$, where $p = 0{\cdot}45$ is the ratio of the diffraction strength of the CrS_6 fragment to the overall diffraction strength; *2*) $|E_{\bar{h}}| > 1{\cdot}5$. From these phases were then calculated in the usual manner further phases for reflections with $|E| \geqq 1{\cdot}05$. The initial phases were refined only in the first cycle and were fixed in further iteration cycles. The overall number of determined and refined phases was 456. After convergence the R_{Karle} value was 0·26and the following E-synthesis indicated the positions of the carbon atoms of all the pentamethylene rings. The maxima corresponding to the positions of the chlorine atoms could again not be distinguished. After 3 refining cycles by the least squares method using the block-diagonal approximation and the isotropic thermal parameters of all the atoms, the structure converged to $R = 0{\cdot}24$. The thermal parameters of all the carbon atoms of the pentamethylene rings had anomalously large values, which probably is the reason for the problems encountered in their localization.

The atoms of both chloroform molecules were then found from differential Fourier synthesis of the residual electron density calculated from the contributions of 625 reflections with $\sin \Theta/\lambda < 0{\cdot}30$.The complete structural model was refined in 6 cycles by the least squares method using the block-diagonal approximation and weights $w = 1$ for $|F_0| \leqq 150$ and $w = 1/|F_0|$ for $|F_0| > 150$ in the minimization of the function $M = \sum w(|F_0| - |F_c|)^2$. Because of the low number of reflections used in the refinement, anisotropic thermal vibrations were assumed only for chlorine atoms in two chloroform molecules. After convergence, the final R value was 0·090 and R_w 0·104($R_w = (\sum w|\Delta F|^2/\sum w|F_0|^2)^{1/2}$). In the final cycle, all the shifts of the positional and thermal parameters were $< 0{\cdot}2\sigma$. The distribution of the minimized M function over the intervals $\sin \Theta/\lambda$ and $|F_0|$ did not exhibit significant fluctuations. The differential Fourier synthesis did not contain maxima higher than 350 $\mathrm{e\,nm^{-3}}$. The usual scattering curves[9] were used in the calculation of the structural factors. The calculations were carried out on the XTL Syntex module and on a Siemens 4004/150 computer using the published programs[10,11].

TABLE II

a The Final Positional and Isotropic Thermal Parameters for the Non-Hydrogen Atoms in the $[Cr(S_2CN(CH_2)_5)_3]$.2 $CHCl_3$ Crystal Structure and Their Standard Deviations (in brackets)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*, nm^2
Cr	0·2224(4)	0·3411(2)	0·3063(1)	0·3 1(1)
		Ligand (1)		
S(11)	0·2705(7)	0·4125(3)	0·3979(3)	0·4 3(1)
S(12)	0·2191(7)	0·2555(3)	0·3915(2)	0·4 0(1)
C(1)	0·2663(23)	0·3290(10)	0·4353(8)	0·2 9(4)
N(1)	0·2988(22)	0·3212(9)	0·4958(8)	0·4 7(4)
C(11)	0·3410(28)	0·3863(13)	0·5345(11)	0·5 2(6)
C(12)	0·2377(31)	0·3882(13)	0·5917(11)	0·6 2(6)
C(13)	0·2363(33)	0·3194(13)	0·6302(1)1	0·6 6(7)
C(14)	0·1923(30)	0·2540(13)	0·5868(10)	0·5 7(6)
C(15)	0·2893(32)	0·2530(14)	0·5275(10)	0·6 2(6)
		Ligand (2)		
S(21)	0·4880(7)	0·3268(3)	0·2812(2)	0·3 9(1)
S(22)	0·2313(7)	0·2511(3)	0·2250(2)	0·3 7(1)
C(2)	0·4302(30)	0·2686(13)	0·2252(11)	0·5 8(6)
N(2)	0·5191(22)	0·2338(10)	0·1844(8)	0·5 5(5)
C(21)	0·6939(33)	0·2565(15)	0·1855(12)	0·7 4(7)
C(22)	0·7837(40)	0·1856(17)	0·1878(14)	0·9 1(8)
C(23)	0·7427(33)	0·1336(13)	0·1366(12)	0·7 7(7)
C(24)	0·5659(37)	0·1115(16)	0·1420(14)	0·8 8(8)
C(25)	0·4705(34)	0·1836(15)	0·1363(13)	0·7 3(7)
		Ligand (3)		
S(31)	0·1876(7)	0·4474(3)	0·2421(2)	0·3 8(1)
S(32)	—0·0513(7)	0·3625(3)	0·3017(3)	0·3 9(1)
C(3)	—0·0059(25)	0·4404(1)	0·2633(9)	0·3 6(5)
N(3)	—0·1076(23)	0·4900(10)	0·2455(8)	0·5 2(5)
C(31)	—0·0650(29)	0·5616(13)	0·2152(11)	0·5 3(6)
C(32)	—0·1611(33)	0·5683(15)	0·1519(13)	0·7 4(7)
C(33)	—0·3382(33)	0·5683(14)	0·1734(12)	0·7 0(7)
C(34)	—0·3655(29)	0·4952(14)	0·2038(11)	0·6 0(6)
C(35)	—0·2756(32)	0·4798(13)	0·2632(11)	0·6 0(6)

TABLE II

(*Continued*)

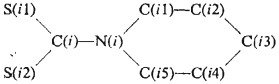
Atom	x/a	y/b	z/c	B, nm^2
		Chloroform (1)		
C(4)	0·1409(42)	0·3440(20)	0·0850(16)	1·1 1(9)
H(1)[a]	0·1500	0·3371	0·1352	
Cl(1)	0·1096(17)	0·2634(6)	0·0468(5)	1·3 3[b]
Cl(2)	0·2979(20)	0·3846(8)	0·0565(7)	1·8 7[b]
Cl(3)	—0·0137(21)	0·4027(7)	0·0627(7)	1·9 3[b]
		Chloroform (2)		
C(5)	—0·1347(36)	0·4795(16)	0·4362(14)	0·8 3(8)
H(2)[a]	—0·0534	0·4435	0·4107	
Cl(4)	—0·1235(11)	0·5686(5)	0·4090(5)	1·1 4[b]
Cl(5)	—0·0998(16)	0·4734(10)	0·5122(5)	1·7 3[b]
Cl(6)	—0·3411(10)	0·4529(5)	0·4294(4)	0·8 9[b]

[a] The positions of the hydrogen atoms in both chloroform molecules were calculated on the basis of the tetrahedral model and distance C—H 0·109 nm. [b] Corresponding isotropic thermal parameters of the chlorine atoms refined by anisotropy.

b The Anisotropic Thermal Coefficients ($\times 10^4$) from the Expression $[\exp -(B_{11}h^2 + \ldots + B_{12}hk + \ldots)]$ for the Chlorine Atoms (standard deviations in brackets)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
			Chloroform (1)			
Cl(1)	799(43)	68(5)	64(4)	31(7)	—134(23)	2(25)
Cl(2)	709(45)	151(9)	103(6)	—250(39)	179(32)	—50(13)
Cl(3)	827(52)	128(8)	106(6)	369(37)	—111(34)	—38(13)
			Chloroform (2)			
Cl(4)	258(18)	74(4)	96(5)	89(17)	— 3(17)	3(8)
Cl(5)	427(31)	264(14)	57(4)	— 42(38)	— 70(21)	—62(14)
Cl(6)	240(16)	58(4)	66(3)	21(14)	40(13)	—25(7)

The final positions and thermal parameters of the nonhydrogen atoms and their standard deviations are given in Table II. The designation of the atoms in the dithiocarbamate ligands is as follows: the sulphur atoms are designated as *S*(ij), where $i = 1$ to 3 is the ligand number and $j = 1$ and 2 designates the sulphur atom in the upper and lower triangle perpendicular to the pseudo-three-fold axis of symmetry of the molecule; the carbon atoms in the pentamethylene rings are designated as C(*ik*), where $k = 1$ to 5 (C(*i*1) is on the same side as the S(*i*1)):



Projection of the unit cell in the direction of the *a*-axis is depicted in Fig. 1.

RESULTS AND DISCUSSION

The molecular structure is depicted schematically in Fig. 2 and the interatomic distances and valence angles in the CrS_6 coordination polyhedron are given in Table III.

All three dithiocarbamate ligands coordinated to the Cr atom are bidentate. The average length of the Cr—S bond is 0·2397 nm, and the lengths of the individual Cr—S bonds do not differ by more than 3σ ($\sigma = 0{\cdot}0006$ nm) from this average value. The equivalence of the metal-sulphur bonds is characteristic for the dithiocarbamates of the transition metals which are not subject to electron type distortion[1-6,12,13].

The CrS_6 coordination polyhedron is markedly distorted from octahedral geometry but has approximately D_3 symmetry: two triangular sides of the polyhedron per-

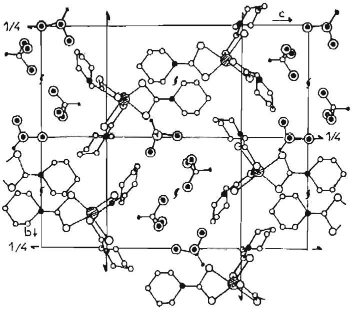


FIG. 1

Projection of the Unit Cell of the $[Cr(S_2CN.(CH_2)_5)_3].2\,CHCl_3$ Crystal Structure onto the (100) Plane pendicular to the pseudo-C_3 symmetry axis and composed of the S(11), S(21), S(31) and S(12), S(22), S(32) (Fig. 2 and 3) atoms are almost parallel (the angle between the planes of these two triangles is 0·5°).

TABLE III

Interatomic Distances and Valence Angles in the CrS_6 Coordination Polhedran (standard deviations are in brackets)

	Interatomic distances, nm		
Cr—S(11)	0·2398(7)	Cr—S(22)	0·2398(6)
Cr—S(12)	0·2405(6)	Cr—S(31)	0·2393(6)
Cr—S(21)	0·2381(6)	Cr—S(32)	0·2408(7)
	Valence angles, °		
S(11)—Cr—S(12)	73·9(2)	S(22)—Cr—S(32)	96·4(2)
S(21)—Cr—S(22)	74·2(2)	S(11)—Cr—S(32)	96·8(2)
S(31)—Cr—S(32)	73·8(2)	S(12)—Cr—S(21)	96·6(2)
S(11)—Cr—S(21)	94·5(2)	S(22)—Cr—S(31)	97·5(2)
S(11)—Cr—S(31)	93·6(2)	S(11)—Cr—S(22)	164·7(2)
S(21)—Cr—S(31)	94·5(2)	S(21)—Cr—S(32)	164·2(2)
S(12)—Cr—S(22)	96·7(2)	S(12)—Cr—S(31)	163·9(2)
S(12)—Cr—S(32)	97·1(2)		

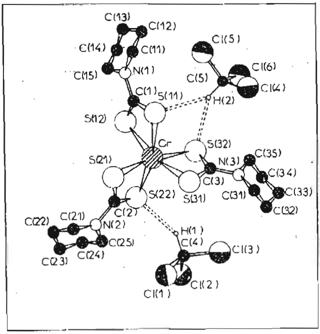


FIG. 2

Schematic Drawing of the $[C(S_2CN(CH_2)_5)_3]$ .2 $CHCl_3$ Molecule as Viewed Along the Pseudo-C_3 Axis of Symmetry

The type and degree of distortion of the tris-bidentate complexes with approximate D_3 symmetry can be described using the angle parameters θ and ψ. Angle θ is defined in Fig. 3 and ψ is the angle between the ligand plane (ligand fragment MS_2) and the C_3 axis. However, the values of angles θ and ψ depend on the definition of the reference C_3 symmetry axis (further designated as $C_{3\mathrm{ref}}$), because the D_3 symmetry of this type of complex is only approximate. To completely analyze the distortion it is useful to define the $C_{3\mathrm{ref}}$ axis so that it is possible to calculate angle parameters θ and ψ individually for each chelate ring, as suggested by Pignolet and coworkers[5]. In this method the $C_{3\mathrm{ref}}$ axis is defined in the following manner: the centres of the segments joining the chelated sulphur atoms of each bidentate ligand are found and the plane passing through these three points is constructed. The $C_{3\mathrm{ref}}$ axis is then defined as the line perpendicular to this plane and passing through the metal atoms. Three values of θ_i and ψ_i corresponding to the three chelate rings for the $[Cr(S_2CN.(CH_2)_5)_3]$ complex are given in Table III. The six-coordinated tris-bidentate complexes with octahedral geometry of the coordination sphere have chelate angles of $\alpha = 90°$, $\phi = 60°$ and $\psi = 35 \cdot 5°$ and mutually orthogonal chelate rings. The $[M(S_2CNR^1R^2)_3]$ complexes cannot attain this geometry because $\alpha \ll 90°$. If the ligands with small chelate rings retained their orthogonality, angle ψ would remain equal to $35 \cdot 3°$, but the ϕ angle would decrease to a value well below 60°. Although the $[M(S_2CNR^1R^2)_3]$ complexes should theoretically retain mutually orthogonal rings, this is not so, as can be seen in Table III, and thus the $[Cr(S_2CNCH_2)_5)_3]$ complex is distorted towards trigonal-prismatic geometry ($\phi = \psi = 0$ for an ideal trigonal prism). The three values of ϕ_i and ψ_i corresponding to the three chelate rings (Table III) are approximately equal, indicating that the distortion of the complex is solely trigonal.

The degree of trigonal distortion of the CrS_6 coordination polyhedron can also be described using various types of S—Cr—S angles, which can be divided into 4 groups: *1*) chelate angle α = S(*i*1)—Cr—S(*i*2) has an average value of 74·0°, *2*) type ξ = = S(*i*1)—Cr—S(*j*1) or S(*i*2)—Cr—S(*j*2) is the angle between the Cr atom and two S atoms in the same triangle, *i.e.* the angle between two Cr—S *cis*-bonds and has

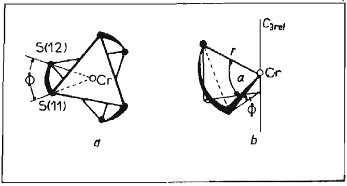


FIG. 3

a Various Views of the CrS_6 Coordination Sphere in the $[Cr(S_2CN(CH_2)_5)_3]$ Complex *b* View along the $C_{3\mathrm{ref}}$ axis (see text) to define angle parameter Φ (projection of chelate angle α onto a plane perpendicular to the $C_{3\mathrm{ref}}$ axis).

an average value of 95·4°. *3*) type $\xi' =$ S(*i*1)—Cr—S(*j*2) is the angle between the metal and two sulphur atoms in two different triangles in the coordination polyhedron, *i.e.* the angle between two Cr—S *cis*-bonds and has an average value of 97·0°. *4*) type $\gamma =$ S(*i*1)—Cr—S(*j*2) is the angle between the Cr atom and two sulphur atoms in two different triangles of the polyhedron which are in *trans*-positions and has an average value of 164·3°. In an ideal octahedron, $\alpha = \xi = \xi' = 90°$, $\gamma = 180°$.

The interatomic distances and valence angles in the dithiocarbamate ligands are given in Tables IV and V. The average values of the bond length in the S_2CNC_2 ligand fragment are: C—S 0·171, S_2C—N 0·133 and CN—C_2 0·149, corresponding to the average values observed for dithiocarbamate complexes, and are consistent with a high degree of π-conjugation in the chelated S_2CN ligand fragments.

The piperidine rings are in the chair conformation and intramolecularly each ring can be identified with the other by application of the pseudo-C_3 axis of symmetry of the coordination polyhedron, *i.e.* the configuration of the piperidine rings does not destroy the $\sim D_3$ symmetry of the coordination sphere (Fig. 2). The average values of the interatomic distances and valence angles in the piperidine rings are: C—C 0·1536 nm and C—C—C 109·5°, fulfilling the requirements of single bonds and tetrahedral hybridization of the carbon atoms.

TABLE IV

Interatomic Distances (nm) and Their Standard Deviations (in brackets) in the Dithiocarbamate (A) Ligands and $CHCl_3$ Molecules (B)

A	Ligand (1), *i* = 1	Ligand (2), *i* = 2	Ligand (3), *i* = 3
S(*i*1)—C(*i*)	0·1 72(2)	0·1 68(2)	0·1 74(2)
S—(*i*2)—C(*i*)	0·1 68(2)	0·1 75(2)	0·1 68(2)
C(*i*)—N(*i*)	0·1 34(2)	0·1 33(2)	0·1 32(2)
N(*i*)—C(*i*1)	0·1 48(3)	0·1 57(3)	0·1 50(3)
N(*i*)—C(*i*5)	0·1 42(3)	0·1 44(3)	0·1 51(3)
C(*i*1)—C(*i*2)	0·1 52(3)	0·1 51(3)	0·1 60(4)
C(*i*2)—C(*i*3)	0·1 50(3)	0·1 49(4)	0·1 60(4)
C(*i*3)—C(*i*4)	0·1 56(3)	0·1 59(4)	0·1 50(3)
C*i*(4)—C(*i*5)	0·1 53(3)	0·1 55(4)	0·1 52(3)

B	Chloroform (1)		Chloroform (2)
C(4)—Cl(1)	0·1 70(3)	C(5)—Cl(4)	0·1 72(3)
C(4)—Cl(2)	0·1 67(4)	C(5)—Cl(5)	0·1 67(3)
C(4)—Cl(3)	0·1 78(4)	C(5)—Cl(6)	0·1 86(3)

The S_2CNC_2 ligand fragments are practically planar (Table VI), but the Cr atom exhibits significant deviation from the planes. This distortion in all three ligands is of the same type and can be described as twisting of the ligand around the axis passing through both chelated sulphur atoms. The angles between the CrS_2 and

TABLE V

The Valence Angles (°) in the Dithiocarbamate Ligands (A) and $CHCl_3$ Molecules (B) (standard deviations in brackets)

A	Ligand (1), $i = 1$	Ligand (2), $i = 2$	Ligand (3), $i = 3$
Cr—S(*i*1)—C(*i*)	84·6(6)	86·7(8)	84·9(7)
Cr—S(*i*2)—C(*i*)	85·0(7)	84·6(8)	85·7(7)
S(*i*1)—C(*i*)—S(*i*2)	116(1)	114(1)	115(1)
S(*i*1)—C(*i*)—N(*i*)	123(1)	127(2)	121(1)
S(*i*2)—C(*i*)—N(*i*)	121(1)	119(2)	124(1)
C(*i*)—N(*i*)—C(*i*1)	121(1)	115(2)	123(2)
C(*i*)—N(*i*)—C(*i*5)	123(1)	127(2)	119(2)
C(*i*1)—N(*i*)—C(*i*5)	116(2)	117(3)	117(2)
N(*i*)—C(*i*1)—C(*i*2)	109(2)	106(2)	108(2)
C(*i*1)—C(*i*2)—C(*i*3)	114(2)	113(2)	106(2)
C(*i*2)—C(*i*3)—3(*i*4)	108(2)	109(2)	106(2)
C(*i*3)—C(*i*4)—C(*i*5)	112(2)	109(2)	114(2)
N(*i*)—C(*i*5)—C(*i*4)	113(2)	109(2)	107(2)
B	Chloroform (1)		Chloroform (2)
Cl(1)—C(4)—Cl(2)	109(2)	Cl(4)—C(5)—Cl(5)	112(2)
Cl(1)—C(4)—Cl(3)	105(2)	Cl(4)—C(5)—Cl(6)	106(2)
Cl(2)—C(4)—Cl(3)	105(2)	Cl(5)—C(5)—Cl(6)	105(2)

TABLE VI

Deviations (in nm × 10^4) of Some Chosen Atoms from the Plane Drawn by the Least Squares Method Through the Conjugated S_2CNC_2 Ligand Fragment

Element	Cr	S(*i*1)	S(*i*2)	C(*i*)	N(*i*)	C(*i*1)	C(*i*5)
Ligand (1), $i = 1$	200	—18	13	3	16	11	—24
Ligand (2), $i = 2$	180	—22	26	5	—34	38	—14
Ligand (3), $i = 3$	330	—39	32	26	—40	51	—30

S_2CNC_2 planes resulting from twisting of the ligand around the S···S axis are 6° for ligands (*1*) and (*2*) and 10° for ligand (*3*). This type of distortion was observed in many dithiocarbamate complexes and is probably a result of crowding due to packing of the molecules in the structure (the S_2CNC_2 ligand fragment tries to retain its planarity because of the high conjugation energy).

Intermolecular interactions of the complex–complex type $<0{\cdot}40$ nm are listed in Table VII. Although the hydrogen atoms of the piperidine rings could not be localized because of the high thermal vibration of the carbon atoms, it is probable that all these interactions are of the S...H—C and C...H—C types, as observed for many other complexes containing dithiocarbamate ligands[14]. The large number of these interactions leads to crowding in the structure and deviations of the Cr atoms from the ligand planes, indicating a relatively high stability of the basic skeleton of the structure formed by the complex molecules. It is apparent from Fig. 1 that channels containing chloroform molecules pass through this basic skeleton, parallel with the crystallographic *a*-axis. In the unit cell each of these channels contains 4 chloroform molecules, which are oriented so that their chlorine atoms fill the space in the centre of the channel and the hydrogen atoms interact with the complex molecules at the channel periphery (the positions of the hydrogen atoms in the chloroform molecules are calculated from the tetrahedral model and the assumed C—H

TABLE VII

Intermolecular Interactions at Distances $<0{\cdot}40$ nm of the Complex–Complex Type

Molecule (1)[a]	Molecule (2)[b]	Distance, nm	Sym. transformation
S(11)	C(24)	0·397	$1 - x, 1/2 + y, 1/2 - z$
S(12)	C(32)	0·356	$-x, 1/2 + y - 1, 1/2 - z$
S(12)	C(33)	0·382	$-x, 1/2 + y - 1, 1/2 - z$
S(21)	C(13)	0·391	$1/2 + x, 1/2 - y, 1 - z$
S(21)	C(14)	0·366	$1/2 + x, 1/2 - y, 1 - z$
S(22)	C(31)	0·394	$-x, 1/2 + y - 1, 1/2 - z$
S(32)	C(14)	0·390	$1/2 + x - 1, 1/2 - y, 1 - z$
C(11)	C(32)	0·384	$1/2 - x, 1 - y, 1/2 + z$
C(12)	C(33)	0·397	$1/2 - x - 1, 1 - y, 1/2 + z$
C(12)	C(32)	0·397	$1/2 - x - 1, 1 - y, 1/2 + z$
C(13)	C(22)	0·395	$1/2 + x - 1, 1/2 - y, 1 - z$
C(22)	C(31)	0·390	$1 - x, 1/2 + y - 1, 1/2 - z$

[a] Basic molecule with atoms with the coordinates given in Table II; [b] symmetrically equivalent molecule related to the basic molecule by the symmetrical transformation given in column 4 of this table.

distance equals 0·109 nm). It is thus probable that slow crystal decomposition is caused by loss of solvent molecules from the channels (which is consistent with the large thermal motion of the chloroform molecules in agreement with Table III) and strong interaction of these molecules with the complex molecules. The differences between the calculated and determined values of the elemental analysis (Table I) and the large thermal vibration of the carbon atoms in the pentamethylene rings can be explained by this process.

It is apparent from Fig. 2 and Table VIII that the strong complex–chloroform interaction is based on the formation of strong hydrogen bonds between the chloroform proton and the sulphur atoms of the dithiocarbamate ligands, where all the S...H distances are less than 0·305 nm, which is the sum of the van der Waals radii of the sulphur and hydrogen atoms[15]. The chloroform molecules are clathrated in the crystal structure so that they approach the complex during the crystallization process roughly along the pseudo-C_2 symmetry axis (the C—H vector is practically colinear with the $\sim C_2$ axis of symmetry of the complex). The S...H interactions are, however, of two types: *1*) H(2) atom of one chloroform molecule forms a symmetrical bifurcated hydrogen bond with two sulphur atoms (Table VIII); *2*) the H(1) atom

TABLE VIII

Intermolecular Interactions at Distances <0·40 nm of the Complex–Chloroform Type

Molecule (1)[a]	Molecule (2)[b]	Distance, nm	Sym. transformation[b]
S(22)	H(1)	0·2 58	—
S(31)	H(1)	0·3 07	—
S(11)	H(2)	0·2 88	—
S(32)	H(2)	0·2 77	—
C(11)	Cl(6)	0·3 76	—
C(12)	Cl(5)	0·3 73	—
C(25)	Cl(1)	0·3 95	—
C(32)	Cl(3)	0·3 79	—
C(35)	Cl(4)	0·3 66	—
C(35)	Cl(6)	0·3 77	—
C(14)	Cl(6)	0·3 78	$1/2 + x, 1/2 - y, 1 - z$
C(23)	Cl(4)	0·3 64	$1 - x, 1/2 + y - 1, 1/2 - z$
C(24)	Cl(6)	0·3 80	$-x, 1/2 + y - 1, 1/2 - z$
C(25)	Cl(4)	0·3 79	$-x, 1/2 + y - 1, 1/2 - z$
C(32)	Cl(5)	0·3 73	$1/2 - x - 1, 1 - y, 1/2 + z - 1$
C(33)	Cl(5)	0·3 59	$1/2 - x - 1, 1 - y, 1/2 + z - 1$

[a,b] Have the same significance as in Table VII.

of the second chloroform molecule interacts with practically only one sulphur atom (the S(31)...H(1) distance is beyond the limit of the can der Waals effects) forming a hydrogen bond which is much stronger than the similar S...H—C intermolecular interaction observed in many well-known structures of dithiocarbamate complexes[14].

It is interesting that the chloroform molecules do not interact with the dithiocarbamate complexes along the molecular pseudo-C_3 axis of symmetry forming a trifurcated hydrogen bond with maximum symmetry of the associate, as has been observed for several stable chloroform solvates of tris-acetylacetonates[16]. However, when the p_π orbitals of the sulphur atoms participate in the interaction with the chloroform hydrogen atoms, this type of association becomes less probable because these orbitals are not oriented along the three-fold axis of symmetry of the complex.

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