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Acta Cryst. (1973). **B29**, 1690

The Crystal Structure of 9-Isobutylthioxanthene*

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(Received 15 February 1973; accepted 12 April 1973)

The crystal structure of 9-isobutylthioxanthene, $C_{17}H_{18}S$, has been determined by the heavy-atom method. The refinement was carried out by the least-squares method with anisotropic temperature factors based on three-dimensional data to give a final R value of 0.059 for 1736 reflections. The space group is $P2_1/n$ with $Z=4$, and the unit-cell parameters are: $a=6.188 \pm 0.002$, $b=28.024 \pm 0.005$, $c=8.426 \pm 0.002$ Å, and $\beta=101.97 \pm 0.03^\circ$. All the hydrogen atoms were located on a difference Fourier synthesis. The crystal contains both enantiomorphs in equal amounts. The best planes of the benzene rings make a dihedral angle of 138.9° . The *meso* atoms C(9) and S are significantly displaced from the benzene ring. The isobutyl group is 'boat axial' with respect to the central thioxanthene ring. All interatomic distances and angles are normal. The sulfur-carbon bond distance is 1.768 ± 0.003 Å. The average carbon-carbon bond distance is 1.522 ± 0.006 Å for carbon-carbon single bonds, 1.386 ± 0.006 Å for carbon-carbon bonds in benzenoid rings and 1.511 ± 0.005 Å for carbon-carbon bonds involving C(9) and the benzenoid ring. The packing of the molecules in the crystal is determined mainly by the van der Waals interaction.

Introduction

9-Isobutylthioxanthene is one of a series of thioxanthene derivatives under study in this laboratory. The objectives of these studies are to determine the conformation of thioxanthene derivatives, the effect of different *meso*- and *peri*-substituents on the stereochemistry of these compounds, and to compare the conformation of thioxanthene derivatives in crystals with that in solution deduced from nuclear magnetic resonance studies. Also, the accurate determination of the C-S bond lengths and the C-S-C bond angles in thioxanthene derivatives will provide information on the bonding characteristic of the sulfur atom.

Experimental

Single crystals of 9-isobutylthioxanthene were obtained through the courtesy of Dr A. L. Ternay of the

Chemistry Department of the University of Texas at Arlington. The crystals are transparent prisms, elongated along the a axis. Accurate cell parameters were measured with Mo $K\alpha$ radiation on a Picker FACS-1 automatic diffractometer. The density of the crystals was determined by the flotation equilibrium method in a mixture of *n*-propyl alcohol and carbon tetrachloride. The crystal data is summarized in Table 1.

Table 1. *Crystal data of 9-isobutylthioxanthene*

Chemical formula $C_{17}H_{18}S$, M.W. 254.40	
Monoclinic, space group $P2_1/n$ from the systematic extinctions:	
$h0l$ absent for $h+l=2n+1$ and $0k0$ absent for $k=2n+1$.	
$a=6.188 \pm 0.002$ Å	$Z=4$
$b=28.024 \pm 0.005$	$D_m=1.202$ g cm $^{-3}$
$c=8.426 \pm 0.002$	$D_x=1.182$
$\beta=101.97 \pm 0.03^\circ$	$\mu(\text{Mo } K\alpha)=2.06$ cm $^{-1}$
	$\lambda(\text{Mo } K\alpha)=0.7107$ Å

The integrated intensity data were collected on a Picker FACS-1 automatic diffractometer. The crystal

* This paper was presented at the ACA meeting, Gainesville, Fla., January 1973.

Table 2. Fractional atomic coordinates and thermal parameters (all $\times 10^4$)

The estimated standard deviations are given in parentheses and refer to the last positions of respective values. The expression for the temperature factor exponent consistent with β values is: $\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	8734 (2)	830 (0)	909 (1)	251 (3)	17 (0)	202 (2)	0 (1)	57 (2)	-6 (1)
C(1)	2835 (7)	643 (2)	-2110 (5)	377 (14)	16 (1)	132 (6)	-13 (2)	31 (8)	2 (2)
C(2)	3224 (8)	259 (2)	-3013 (5)	528 (19)	16 (1)	132 (7)	-18 (3)	11 (9)	-5 (2)
C(3)	5282 (9)	44 (2)	-2754 (5)	571 (20)	13 (1)	162 (7)	-4 (3)	103 (10)	-5 (2)
C(4)	6971 (7)	229 (1)	-1536 (5)	423 (15)	14 (1)	176 (7)	5 (2)	104 (9)	4 (2)
C(5)	8207 (7)	1023 (2)	3969 (5)	380 (14)	15 (1)	172 (7)	0 (2)	1 (8)	3 (2)
C(6)	7039 (9)	1182 (2)	5100 (5)	532 (20)	21 (1)	133 (7)	-7 (3)	23 (10)	1 (2)
C(7)	4926 (8)	1353 (2)	4610 (5)	503 (18)	19 (1)	148 (7)	-6 (3)	99 (9)	-7 (2)
C(8)	3981 (6)	1381 (2)	2979 (5)	366 (13)	14 (1)	147 (6)	-3 (2)	85 (7)	0 (2)
C(9)	4098 (6)	1282 (1)	20 (4)	250 (10)	14 (1)	127 (6)	4 (2)	47 (6)	4 (1)
C(11)	4489 (6)	840 (1)	-904 (4)	301 (11)	12 (1)	133 (6)	-6 (2)	64 (7)	2 (1)
C(12)	6562 (6)	611 (1)	-634 (4)	311 (12)	11 (1)	144 (6)	-5 (2)	75 (7)	-1 (1)
C(13)	7235 (6)	1047 (1)	2323 (4)	295 (12)	13 (1)	142 (6)	-5 (2)	36 (7)	-1 (1)
C(14)	5118 (6)	1238 (1)	1809 (4)	281 (11)	11 (1)	140 (6)	-4 (2)	62 (6)	1 (1)
C(15)	4895 (7)	1733 (1)	-733 (5)	358 (13)	14 (1)	153 (6)	8 (2)	84 (7)	7 (2)
C(16)	4192 (8)	2203 (2)	-128 (5)	465 (17)	15 (1)	200 (8)	16 (3)	98 (9)	9 (2)
C(17)	1706 (10)	2265 (2)	-453 (9)	551 (23)	22 (1)	471 (17)	44 (4)	222 (16)	25 (3)
C(18)	5284 (10)	2616 (2)	-836 (8)	695 (26)	14 (1)	421 (15)	10 (4)	238 (16)	18 (3)

was cut to approximately $0.28 \times 0.45 \times 0.32$ mm in dimensions and was mounted along the *b* axis. A $\theta/2\theta$ scanning mode with Mo *K* α radiation was used to measure 2549 independent reflections with 2θ values below 50° , of which 1736 reflections were considered as observed. The total time for the background counts recorded at the limits of each scan was 20 sec. A reflection was considered observed if its intensity was greater than $3\sigma(I)$, where $\sigma(I)$ is determined from counting statistics. Three standard reflections were repeated in intervals of every 100 reflections, and their intensities showed fluctuations of less than 7% over the data collection period. Scale factors, based on the variation of the standard reflections, were applied to the intensity data to compensate for this fluctuation. The intensity data were reduced to structure factors by the application of Lorentz and polarization factors, and no absorption corrections were applied.

Determination and refinement of the structure

The structure was solved by the heavy-atom method. The positions of the sulfur atoms were obtained from the Harker peaks (u, v, w) , $(\frac{1}{2}, v, \frac{1}{2})$, and $(u, \frac{1}{2}, w)$ of the $E^2 - 1$ Patterson synthesis. The phases for the first Fourier synthesis were based on the structure factor calculation ($R=0.58$) from the positions of sulfur atoms. All carbon atoms were distinctly located in the first Fourier synthesis. The structure factor calculation for all atoms except hydrogen yielded an *R* value of 0.31 for the three-dimensional data. Two cycles of full-matrix least-squares refinement with isotropic temperature factors reduced *R* to 0.147. Two cycles of full-matrix least-squares refinement with anisotropic temperature factors reduced *R* to 0.097. All hydrogen atoms were clearly revealed in the difference Fourier synthesis with reasonable bond length and bond angles with respect to the atoms to which they are bonded. Two more cycles of least-squares refinement with an-

Table 2 (cont.)

Hydrogen atomic coordinates ($\times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>
H(C1)	148 (9)	80 (2)	-207 (6)
H(C2)	188 (10)	12 (2)	-381 (7)
H(C3)	553 (10)	-21 (2)	-339 (7)
H(C4)	846 (9)	3 (2)	-124 (7)
H(C5)	968 (9)	83 (2)	435 (6)
H(C6)	734 (10)	104 (2)	621 (7)
H(C7)	412 (10)	148 (2)	545 (7)
H(C8)	265 (9)	154 (2)	269 (7)
H(C9)	256 (8)	135 (2)	-12 (6)
H(C15)1	644 (9)	175 (2)	-56 (6)
H(C15)2	431 (9)	177 (2)	-189 (7)
H(C16)	457 (10)	214 (2)	96 (7)
H(C17)1	137 (11)	215 (3)	-169 (10)
H(C17)2	159 (11)	263 (3)	-11 (9)
H(C17)3	82 (11)	199 (3)	0 (10)
H(C18)1	474 (12)	295 (2)	-50 (9)
H(C18)2	475 (13)	254 (2)	-215 (10)
H(C18)3	677 (13)	259 (3)	-78 (10)

isotropic temperature factors, including all the hydrogen atoms, gave the final *R* value of 0.059. The positional parameters of the hydrogen atoms were refined, but their thermal parameters were assigned the same as those of the atoms to which they are bonded. Cruickshank's (1965) weighting scheme was used in order to make $[\sum w(F_o - F_c)^2 / (\text{no. of reflections} - \text{no. of parameters})]^{1/2}$ approximately equal to unity, and the average $w(F_o - F_c)^2$ is approximately constant for different magnitudes of $|F_o|$ and $\sin \theta$. The weight of the reflection was calculated according to the formula $1/w = (2.75 - 0.25|F_o| + 0.0075|F_o|^2)$. The final positional and thermal parameters are listed in Table 2, and the corresponding structure factors are given in Table 3.

The computer programs used in this analysis were the Busing, Martin & Levy *ORFLS* program modified by Shiono (1970), a modified Zalkin Fourier Synthesis program (Shiono, 1967), the data reduction program of Shiono (1971), and a number of structure interpreta-

Table 3 (cont.)

Table 3 (cont.) data table with multiple columns of numerical values and labels.

tion programs (Shiono, 1971; Chu, 1971). All calculations were carried out on a UNIVAC 1108 computer.

Description of the structure

The configuration of a 9-isobutylthioxanthene molecule and the identification of the atoms are shown in the ORTEP (Johnson, 1965) drawing, Fig. 1. Since the crystal belongs to a centrosymmetric space group, both enantiomorphs are present in the crystal.

The bond lengths and bond angles with their standard deviations are shown in Fig. 2. The C-C bond lengths within the benzene rings range from 1.366 to 1.401 Å with a mean value of 1.386 ± 0.006 Å. The C-C bond length involving C(9) of the central ring are 1.509 ± 0.005 Å and 1.512 ± 0.005 Å. The C-C bond lengths in the isobutyl group and that between C(9) and the exocyclic carbon range from 1.508 to 1.541 Å with a mean value of 1.522 ± 0.006 Å. The mean value of the two carbon-sulfur bond lengths is 1.768 ± 0.003

Å. All of these bond lengths are in good agreement with the results obtained in methixene (Chu, 1972). The average carbon-hydrogen bond length is 1.00 ± 0.03 Å, which is in agreement with the values obtained in other X-ray crystal structure analyses.

The valence angles in the benzenoid rings are normal. The least-squares planes in 9-isobutylthioxanthene are shown in Table 4. The central ring is in a boat conformation, and the displacements of C(9) and S are on the opposite side of the benzene planes which has also been found in methixene (Chu, 1972). The dihedral angle between the least-squares planes of the two benzene rings is 138.9° compared with 137.9° in methixene and 127.2° in cis-9-methylthioxanthene 10-oxide (Jackobs & Sundaralingam, 1969). The isobutyl group is 'boat axial' with respect to the central thioxanthene ring and the same conformation was observed for the piperidyl methyl group in methixene. In cis-9-methylthioxanthene, however, the methyl group was found to be in 'boat equatorial' conformation. The difference in conformation of the C(9) substituents and the difference of coordination number of sulfur atoms are presumably responsible for the difference in dihedral angle between 9-isobutylthioxanthene and cis-9-methylthioxanthene 10-oxide. The n.m.r. studies on the meso C(9) substituted methyl, ethyl, isopropyl, and t-butyl derivatives of thioxanthene (Ternay & Evans, 1970) indicated that the

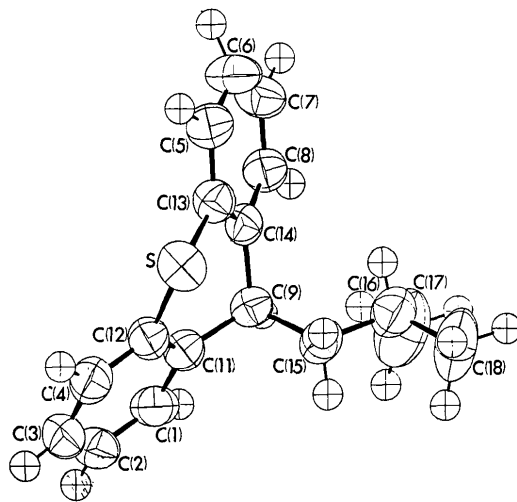


Fig. 1. The structure of one asymmetric unit of 9-isobutyl thioxanthene. The diagram has been produced by the ORTEP program (Johnson, 1965).

Table 4. Least-squares planes and the displacements of atoms from the plane

Equation of planes: Ax + By + Cz = D, where x, y, z are in Å referred to the monoclinic axes.

Plane	A	B	C	D
(a)	0.4221	0.6142	-0.7408	3.1708
(b)	0.4366	0.6013	-0.7462	3.2106
(c)	0.3914	0.9195	-0.1171	4.2338
(d)	0.4085	0.9122	-0.1163	4.2759
(e)	0.4796	0.7929	-0.4686	3.5553

Dihedral angles between the least-squares planes

Planes	Dihedral angle
(a) and (c)	138.9°
(b) and (d)	138.4
(a) and (b)	1.1
(c) and (d)	1.1

Table 4 (cont.)

Displacements in Å from the least-squares planes

	Benzene ring				Central ring		
	(a)	(b)	(c)	(d)	(e)		
C(1)	-0.006	-0.034	C(5)	-0.002	0.025	C(11)	0.001
C(2)	-0.002	-0.008	C(6)	0.013	0.025	C(12)	-0.001
C(3)	0.004	0.022	C(7)	-0.009	-0.024	C(13)	0.001
C(4)	0.003	0.024	C(8)	-0.005	-0.032	C(14)	-0.001
C(11)	0.012	-0.014	C(13)	-0.013	0.002	S	0.522*
C(12)	-0.011	-0.010	C(14)	0.016	0.004	C(9)	0.502*
S	-0.029*	-0.024	S	-0.070*	-0.036		
C(9)	0.093*	0.044	C(9)	0.060*	0.036		

* Indicates atoms excluded from the calculation of the least-squares planes.

methyl derivative is conformationally inhomogeneous and that ethyl, isopropyl, and t-butyl derivatives are essentially 'boat-axial' conformation. The results obtained in this study are in agreement with those observed in solution. The torsion angles of the isobutyl group are shown in Fig. 3; this group is in a staggered ar-

angement. (The torsion angles were calculated from the coordinates for the enantiomorph given in Table 2. The enantiomeric structure will have the torsion angles of the same magnitude but of opposite direction.)

The packing of the molecules in the crystal projected down the *a* axis is shown in Fig. 4. There are no inter-

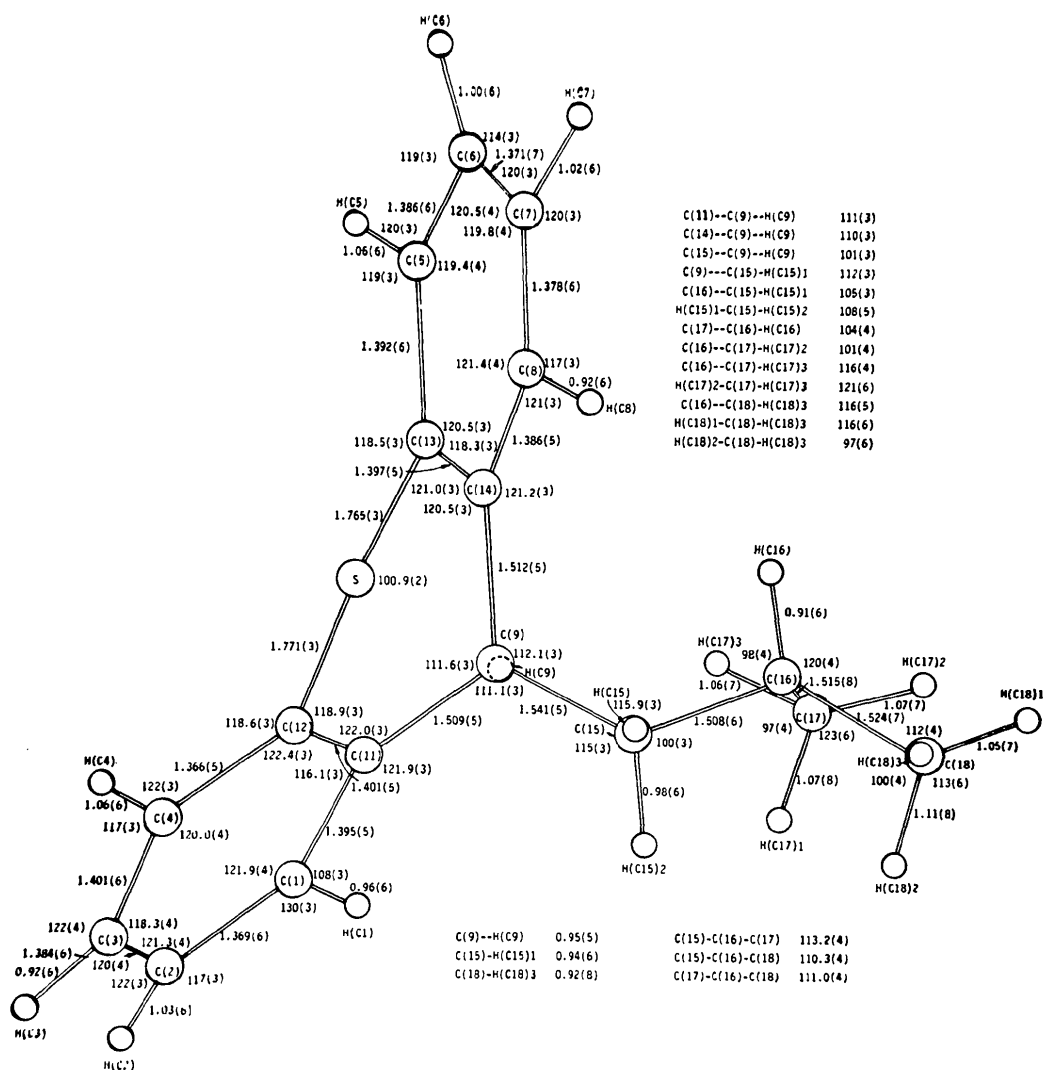


Fig. 2. Bond distances and bond angles of 9-isobutylthioxanthene.

molecular contacts less than van der Waals distances. The closest intermolecular distance between C(3) and C(13) is 3.485 Å.

Analysis of thermal motion

The rigid-body thermal analysis of the eighteen non-hydrogen atoms was carried out by the method of Schomaker & Trueblood (1968). The values of **T**, **L**, and **S** tensors together with their standard deviations are shown in Table 5. The r.m.s. amplitude of the principal axes of **T**, **L**, and **S** and their direction cosines

with respect to orthogonal axes *a*, *b*, and *c** are also given in Table 5. The r.m.s. value of ΔU_{ij} , the difference between observed U_{ij} and calculated U_{ij} based on the rigid-body model, is 0.0072 Å². A comparison of this value with the mean σU_{ij} value of 0.0031 Å², calculated from the estimated standard deviation of the β_{ij} of the least-squares refinement, indicates that the rigid-body model is only moderately satisfactory.

Table 5. Rigid-body thermal parameters referred to orthogonal axes *a*, *b*, *c**

Estimated standard deviations of the elements of the **T**, **L**, and **S** tensors are given in parentheses. **T** is in Å² × 10³, **L** in deg² and **S** in deg Å × 10³.

$$\mathbf{T} = \begin{pmatrix} 43(3) & 1(2) & 4(2) \\ & 45(2) & 6(2) \\ & & 46(2) \end{pmatrix} \quad \mathbf{L} = \begin{pmatrix} 9.9(9) & 2.3(11) & -2.9(10) \\ & 15.5(18) & 1.2(16) \\ & & 12.0(17) \end{pmatrix}$$

$$\mathbf{S} = \begin{pmatrix} 60(57) & 11(23) & 229(29) \\ -46(46) & 57(74) & -17(40) \\ -46(46) & -92(40) & -120(460)^* \end{pmatrix}$$

* The trace of **S** has been set to zero, e.s.d. of deleted $S(3,3)$ is given.

Principal axes of **T**

Eigenvalues (Å)	Direction cosines (× 10 ³)		
0.229	332	596	731
0.206	819	-568	87
0.196	468	571	-675

Principal axes of **L**

Eigenvalues (deg)	Direction cosines (× 10 ³)		
4.04	-315	-948	-55
3.75	-532	104	840
2.66	-792	301	-531

Principal axes of **S**

Eigenvalues (deg Å)	Direction cosines (× 10 ³)		
0.120	617	-605	507
0.040	-633	-771	-94
-0.155	464	-236	-850

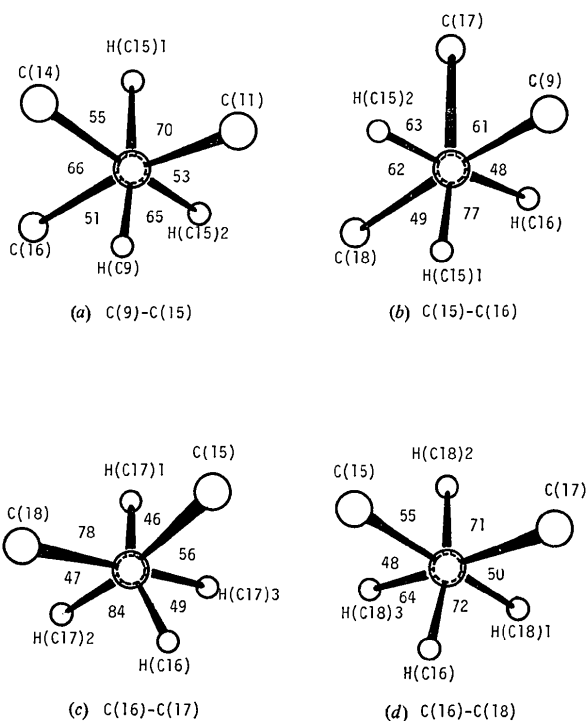


Fig. 3. The torsion angles about the (a) C(9)-C(15), (b) C(15)-C(16), (c) C(16)-C(17), and (d) C(16)-C(18) bonds.

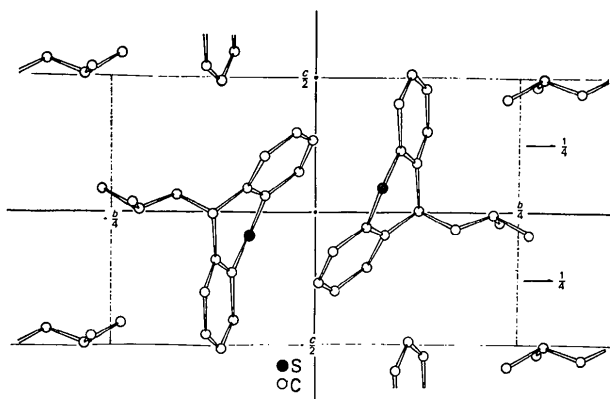


Fig. 4. The molecular packing diagram, excluding hydrogen atoms, viewed down the *a* axis of 9-isobutylthioxanthene.

This research was supported by the Robert A. Welch Foundation, Houston, Texas. The author wishes to thank Dr John Wainwright of NASA, Houston for his assistance in obtaining the diffraction data from the automatic diffractometer in his laboratory, Dr R. Shiono of the University of Pittsburgh for making the ORTEP plot and the rigid-body thermal analysis calculation, and Dr A. L. Ternay Jr for kindly supplying the crystals.

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Acta Cryst. (1973). **B29**, 1696

Etude Structurale des Hydroxynitrates de Nickel et de Zinc.

I. Classification Structurale

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(Reçu le 23 février 1973, accepté le 26 mars 1973)

The theoretical structural study of the hydroxynitrates $xM(OH)_2 \cdot yM(NO_3)_2 \cdot zH_2O$ ($M = Ni, Zn$) based on the only hypothesis that their structure proceeds from that of the related hydroxides $M(OH)_2$, leads to two main structural types. These basic nitrates can be characterized by a stacking of sheet sequences of formula MX_{2+m} with $m = z/(x+y)$ and $X = OH^-, H_2O, NO_3^-$. The first structural type occurs when m is a positive integer (hydrated salts) or zero (anhydrous salts). There is, therefore, for hydrated salts a deficiency of cations with respect to the sheets MX_2 characteristic of hydroxides $M(OH)_2$. Each sheet consists of $(2+m)$ hexagonal close packed layers, and the cations M occupy some of the octahedral holes. The second structural type occurs when m is not an integer; this produces the formation of layers not close packed. Then, each sheet comprises two hexagonal close packed layers and two layers not close packed, the cations M occurring at both octahedral and tetrahedral holes. The characteristics of each structural type are described together with x, y and z values consistent with the proposed models. The conclusions of this study are in excellent agreement with known structures. The systematic classification proposed enables one to predict, *a priori*, the formulae and structures of hydroxynitrates which are structurally derived from $M(OH)_2$.

Introduction

Depuis les importants travaux de synthèse entrepris par Feitknecht (1930, 1933, 1940) sur les hydroxynitrates de zinc et de nickel, de formule générale $xM(OH)_2 \cdot yM(NO_3)_2 \cdot zH_2O$ ($M = Ni$ ou Zn), peu de déterminations structurales ont été effectuées sur ces sels, vraisemblablement en raison de leur cristallisation souvent imparfaite. Seules ont été résolues récemment la structure de $xNi(OH)_2 \cdot Ni(NO_3)_2$ ($2 \leq x \leq 3$) (Gallezot & Prettre, 1969) à partir du diagramme de poudre, et celle de $4Zn(OH)_2 \cdot Zn(NO_3)_2 \cdot 2H_2O$ à l'aide d'un monocristal (Stählin & Oswald, 1971).

Ces nitrates basiques évoluant par hydrolyse vers l'hydroxyde correspondant $M(OH)_2$, Feitknecht (1953) avait émis l'hypothèse selon laquelle la plupart d'entre eux auraient une structure lamellaire dérivant de celle des hydroxydes par remplacement de certains ions OH^- par des ions NO_3^- .

Dans le cadre d'une étude structurale des nitrates basiques de zinc et de nickel, il nous a paru intéressant d'essayer, sur la base des hypothèses de Feitknecht, de prévoir les types structuraux possibles, d'en effectuer

une classification systématique en fonction des coefficients x, y et z et de déterminer les relations entre les évolutions physico-chimiques et structurales.

L'article I de cette série rend compte de la classification structurale a priori des nitrates basiques de zinc et de nickel. Le seul principe de base de cette classification est la recherche de la conservation totale ou presque totale, du réseau anionique de type hexagonal compact caractéristique des hydroxydes cristallisant dans le type brucite. D'une manière générale, dans la suite de cet article, la lettre X symbolisera un atome d'oxygène appartenant soit aux ions OH^- ou NO_3^- , soit aux molécules d'eau; le cas échéant, la signification exacte de X sera précisée.

I. Position du problème

Les hydroxydes $Ni(OH)_2$ (Natta, 1928) et $\alpha Zn(OH)_2$ (Feitknecht, 1932) ont une structure lamellaire caractéristique du type brucite $Mg(OH)_2$. Les ions hydroxydes OH^- forment un assemblage hexagonal compact, les cations occupant les sites octaédriques à raison d'un plan cationique sur deux totalement lacunaire. Le