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Acta Cryst. (1974). B**30**, 1053

The High-Temperature Structure of $CsCuCl_3$

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(*Received* 15 *October* 1973; *accepted* 29 *November* 1973)

The crystal structure of $CsCuCl_3$, above its transition temperature (423°K) has been determined at 466°K. The polar hexagonal space group $P6_3mc$ is the most probable one for this compound. The cell dimensions are $a=7{\cdot}245$ (7) and $c=6{\cdot}150$ (6) Å with $Z=2$. Full-matrix least-squares refinement of 185 observed symmetry-independent three-dimensional diffractometer data (Mo $K\alpha$) led to a final R index on F of 0·041 and a weighted R index of 0·069. Above its transition temperature $CsCuCl_3$ is isostructural with $CsCrCl_3$ and $CsCrBr_3$. The Cu^{2+} ion is slightly displaced from the centre of a Cl^- octahedron along the trigonal axis (c axis) giving rise to a ferroelectric structure.

Introduction

In a previous communication (Kroese, Tindemans-van Eyndhoven & Maaskant, 1971) we reported a phase transition in $CsCuCl_3$ at 423°K; we also discussed the high-temperature structure as determined by single-crystal Weissenberg measurements. However, owing to the lack of sufficient data we could not determine unequivocally the space group of this compound. In order to solve this problem we performed single-crystal X-ray diffractometer measurements, the results of which are communicated here.

Experimental

Crystals of $CsCuCl_3$ were grown from an aqueous solution as described elsewhere (Schlueter, Jacobson & Rundle, 1966). An irregularly shaped crystal of approximate size $0{\cdot}2\times0{\cdot}2\times0{\cdot}6$ mm was mounted on an Enraf–Nonius three-circle single-crystal diffractometer with the hexagonal axis along the φ-axis. The diffractometer was equipped with an apparatus enabling us to heat the crystal with a continuous stream of hot nitrogen gas. The temperature of the crystal during the experiment was 466 ± 5°K. Precise unit-cell parameters were determined at this temperature by measuring nine carefully selected reflexions with Zr-filtered Mo $K\alpha$ radiation ($\lambda=0{\cdot}71069$ Å). The cell parameters are: $a=7{\cdot}245$ (7), $c=6{\cdot}150$ (6) Å (numbers in parentheses here and in the tables are estimated standard deviations in the least significant digit). The calculated density at 466°K for $Z=2$ and a molecular weight of 302·8, $d=3{\cdot}63$ g cm^{-3}, agrees with the measured density at room temperature, $d=3{\cdot}65$ g cm^{-3}. Intensities were recorded by the θ–2θ scan method for all reflexions with θ between 4 and 30° using Zr-filtered Mo $K\alpha$ radiation. The scan angle Δ was 1·7°. The counting time was 41 s for each background and 82 s for the scan. In all 1039 reflexions were measured. The standard deviations σ_F were calculated from the statistical inaccuracy of the measurement with an amount added for errors in the absorption correction and attenuation factors. Reflexions with intensity less than twice the standard deviation were considered not significant.

All data were corrected for absorption,* Lorentz and polarization effects. The transmission factors ranged between 0·20 and 0·28 (μ = 119·7 cm^{-1}).

Determination of the structure

The crystal belongs to the hexagonal Laue group $6/mmm$. Together with the systematic absences $hh\overline{2h}l$, $l=2n+1$ this indicates one of the following space groups: $P6_3/mmc$, $P\bar{6}2c$ or $P6_3mc$. Models having these space groups were refined by a full-matrix least-squares method. Scattering factors for Cs^+, Cu^{2+} and Cl^- and anomalous dispersion corrections ($\Delta f'$ and $\Delta f''$) for Cs^0, Cu^0 and Cl^0 were taken from the compilation of Cromer & Waber (1965). All intensities were reduced to F values and an averaging procedure was carried out for each space group giving only symmetry-independent reflexions: only the significant reflexions were used in the refinement. The function minimized during the least-squares refinement process was: $\sum w_F(|F_o|-|F_c|)^2$ with the weighting factor $w_F=1/(\sigma_F)^2$. Discrepancy indices referred to are:

$$R_F=\frac{\sum||F_o|-|F_c||}{\sum|F_o|}$$

and

$$R_{wF}=\left[\frac{\sum w_F(|F_o|-|F_c|)^2}{\sum w_F|F_o|^2}\right]^{1/2}.$$

Assuming 2 molecules per unit cell the possible positions for the atoms in the three space groups can easily be found in *International Tables for X-ray Crystallography* (1952); they are given in Table 1.

Table 1. *Positions for the atoms in the different space groups*

	$P6_3/mmc$				$P\bar{6}2c$				$P6_3mc$			
Cs	(*d*)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	(*d*)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	(*b*)	$\frac{1}{3}$	$\frac{2}{3}$	z
Cu	(*a*)	0	0	0	(*a*)	0	0	0	(*a*)	0	0	z
Cl	(*h*)	x	$2x$	$\frac{1}{4}$	(*h*)	x	y	$\frac{1}{4}$	(*c*)	x	$2x$	z

The positional parameters and anisotropic thermal parameters for all atoms and a scaling factor were refined. In the refinement of the model with space group $P6_3mc$ the z coordinate of the Cs atom was set at $\frac{3}{4}$.

Table 2. *Final discrepancy values*

	R_f	R_{wf}	Number of reflexions	Number or parameters	ERF
$P6_3/mmc$	0·059	0·101*	145	9	10·81
$P\bar{6}2c$	0·066	0·105	276	11	7·80
	0·059	0·100*	145	11	10·84
$P6_3mc$	0·041	0·069	185	12	6·54
	0·046	0·068*	145	12	7·32

* Values used with Hamilton's test.

The final discrepancy indices for the refinements are given in Table 2. The estimated standard deviations of an observation of unit weight (ERF) given by $[\sum w_F(|F_o|-|F_c|)/(NO-NV)]^{1/2}$ (where NO is the number of observations and NV is the number of variables) are also given in Table 2. The values are probably high owing to systematic errors in the absorption correction, which had to be carried out for an imaginary crystal form that corresponded with the measured transmission curve for the main reflexions 002 and 004, because the shape of the single crystal was too irregular. The errors in the absorption correction are also thought to be the explanation for some positive and negative peaks around the threefold axes of the system in the final difference Fourier synthesis. Least-squares refinements for all three models were also carried out with the set of 145 symmetry-independent reflexions of the space group $P6_3/mmc$. The final discrepancy indices for these refinements are also given in Table 2. When we apply Hamilton's (1965) statistical test to these R indices we find that the possibility of $P6_3/mmc$ or $P\bar{6}2c$ being the

Table 3. *Positional and thermal parameters for* $CsCuCl_3$(466°K) *with the space group* $P6_3\,mc$

The general anisotropic temperature factor has the form $[\exp -2\pi^2(\sum_{i,j} U_{ij}a_i^*a_j^*)]$.

Owing to the site symmetry of the ions there are several restrictions on the thermal parameters U_{ij}:

Cu, Cs: $U_{11}=U_{22}=2U_{12}$ $U_{13}=U_{23}=0$
Cl: $U_{22}=2U_{12}$ $2U_{13}=U_{23}$

All parameters not given as fractions are multiplied by 10^3.

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Cs	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	52 (1)	52 (1)	92 (2)	52 (1)	0	0
Cu	0	0	15 (6)	65 (1)	65 (1)	44 (2)	65 (1)	0	0
Cl	152 (3)	304 (6)	280 (15)	59 (2)	70 (3)	116 (6)	70 (3)	36 (14)	18 (7)

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* All calculations were carried out on the Leiden University I.B.M. 360/50 and later on the 360/65 computer using programs written or modified by Mrs Rutten-Keulemans and Mr De Graaff of the section X-ray and electron diffraction.

right space group can be rejected on a significance level less than 0·5 %. So on this basis of the statistical test we conclude that the structure of $CsCuCl_3$ at 466°K (*i.e.* above its transition temperature) has the polar space group $P6_3mc$ with parameters as given in Table 3. A list of structure factors can be found in Table 4.

Our calculations show that $CsCuCl_3$ above its transition temperature is not isostructural with $CsNiCl_3$ (Tishchenko, 1955) and $CsMgCl_3$ (McPherson, Kistenmacher & Stucky, 1970) the main difference being that the centre of inversion on the Cu^{2+} ion is lacking. The coordination about the Cu^{2+} ion is no longer octahedral with a slight trigonal distortion (site symmetry D_{3d}): the Cu^{2+} ion is displaced along the c axis towards a shared face. This results in a lowering of the site symmetry from D_{3d} to C_{3v} and also in the possibility of different Cu–Cl distances.

Table 4. *List of structure factors* × 10

$F(0,0,0)$ on this scale is 2706.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-1	2	0	1110	1112	2	-8	0	58	59	0	1	2	644	627	0	-2	-3	630	619	0	7	4	30	34
1	-2	0	1089	1112	-1	8	0	147	159	0	-1	-2	637	630	-1	3	3	238	252	-4	8	4	126	115
0	2	0	333	332	1	-8	0	153	159	-1	2	2	221	184	1	-3	-3	233	258	-1	8	4	65	75
0	-2	0	329	332	-1	9	0	111	110	1	-2	-2	219	196	0	3	3	90	90	0	1	5	131	153
0	3	0	741	797	1	-9	0	113	110	0	2	2	918	904	-1	4	3	253	256	0	2	5	196	207
0	-3	0	749	797	5	-10	0	96	97	0	-2	-2	898	900	0	4	3	374	363	-1	3	5	96	112
-2	4	0	1231	1248	0	1	1	631	604	-1	3	2	603	605	-2	5	3	208	210	0	3	5	38	31
2	-4	0	1185	1248	0	-1	-1	621	604	1	-3	-2	586	606	-1	5	3	48	47	-1	4	5	104	107
-1	4	0	82	80	0	2	1	1222	1221	0	3	2	157	133	0	5	3	100	105	0	4	5	114	124
1	-4	0	84	80	0	-2	-1	1209	1214	0	-3	-2	151	144	-2	6	3	245	230	-2	5	5	81	90
0	4	0	178	169	-1	3	1	377	372	-2	4	2	512	468	-1	6	3	136	144	0	5	5	37	53
0	-4	0	189	169	1	-3	-1	373	377	2	-4	-2	493	461	-3	7	3	74	81	-2	6	5	70	64
-2	5	0	145	161	0	3	1	219	156	-1	4	2	395	387	-2	7	3	42	47	-1	6	5	68	[illegible]
2	-5	0	145	161	0	-3	-1	205	166	1	-4	-2	375	389	-1	7	3	102	101	-3	7	5	42	[illegible]
-1	5	0	494	513	-1	4	1	389	397	0	4	2	521	507	0	7	3	74	78	-1	7	5	43	44
1	-5	0	498	513	1	-4	-1	386	401	-2	5	2	230	214	-3	8	3	94	90	-1	8	5	34	34
0	5	0	73	79	0	4	1	626	631	-1	5	2	124	122	-2	8	3	93	91	0	0	6	24	35
0	-5	0	78	79	0	-4	-1	607	627	0	5	2	316	315	0	8	3	72	60	0	1	6	154	156
-3	6	0	439	444	-2	5	1	315	323	-3	6	2	134	137	-4	9	3	50	54	-1	2	6	36	26
3	-6	0	421	444	-1	5	1	73	79	-2	6	2	293	291	0	0	4	796	796	0	2	6	101	106
-2	6	0	96	95	0	5	1	144	141	-1	6	2	234	228	0	0	-4	790	786	-1	3	6	142	132
2	-6	0	92	95	-2	6	1	385	388	0	6	2	195	187	0	1	4	174	179	0	3	6	36	60
-1	6	0	27	43	-1	6	1	190	201	-3	7	2	196	145	0	-1	-4	171	180	-1	4	6	112	95
1	-6	0	35	43	0	6	1	29	16	-2	7	2	73	62	-1	2	4	464	451	0	4	6	133	133
0	6	0	423	439	-3	7	1	100	113	-1	7	2	103	100	0	2	4	41	27	-2	5	6	76	67
0	-6	0	431	439	-2	7	1	62	77	0	7	2	59	62	-1	3	4	85	97	0	5	6	86	71
-3	7	0	57	54	-1	7	1	142	153	-4	8	2	128	124	0	3	4	342	364	-2	6	6	54	63
3	-7	0	59	59	0	7	1	111	117	-3	8	2	108	107	-2	4	4	492	466	-1	6	6	69	56
-2	7	0	231	233	-3	8	1	126	137	-2	8	2	133	124	-1	4	4	79	49	-3	7	6	56	47
2	-7	0	235	233	-2	8	1	151	150	-1	8	2	57	65	0	4	4	22	19	0	1	7	37	62
-1	7	0	30	19	0	8	1	109	128	0	8	2	69	65	-2	5	4	100	99	0	2	7	35	46
1	-7	0	18	19	-4	9	1	77	80	-4	9	2	43	36	-1	5	4	257	239	-1	3	7	31	33
0	7	0	44	57	-2	9	1	36	33	-2	9	2	69	71	-3	6	4	233	207	-1	4	7	30	50
0	-7	0	43	57	-1	9	1	43	50	-1	9	2	56	53	-2	6	4	27	11	0	0	8	72	76
-4	8	0	291	277	-4	10	1	75	70	0	1	3	376	373	0	6	4	194	179	0	1	8	43	45
4	-8	0	276	277	0	0	2	933	939	0	-1	-3	368	378	-2	7	4	125	115	-1	2	8	70	61
-2	8	0	57	59	0	0	-2	943	929	0	2	3	647	627	-1	7	4	35	24	0	3	8	56	68

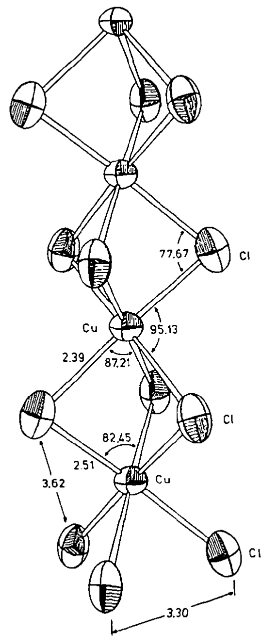

Fig. 1. A perspective view of the anionic chain of $CsCuCl_3$.

In fact we determined three shorter distances of 2·39 (1) Å and three larger distances of 2·51 (1) Å but in reality the difference between the distances may be smaller. A list of nearest-neighbour bond lengths and relevant angles is given in Table 5. The distances and angles are indicated in Fig. 1.

Table 5. *Interionic distances* (Å) *and bond angles and their estimated standard deviations*

The e.s.d.'s include the e.s.d.'s in the cell parameters.

Distances		Bond angles	
Cu–Cl	2·51 (1)	Cl–Cu–Cl	82·5 (4)
Cu–Cl′	2·39 (1)		
		Cl′–Cu–Cl′	87·2 (5)
Cl–Cl	3·30 (1)		
Cl–Cl′	3·619 (4)	Cl–Cu–Cl′	95·1 (2)
Cs–Cl	3·68 (1)	Cu–Cl–Cu	77·7 (2)
Cs–Cl′	3·632 (4)		

With the parameters given in Table 3 and assuming a point-charge model we can calculate a spontaneous polarization $P_s = -4{\cdot}2 \times 10^{-2}$ C m^{-2} for $CsCuCl_3$ at 466°K. In order to check the results of the structure determination independently polarization measurements were made but no conclusive evidence for the polarity or non-polarity of the space group could be obtained.

A possible explanation for the ferroelectric behaviour may be the following: owing to the lowering of the symmetry of the ions, especially Cl^- and Cu^{2+}, more orbitals can be involved in the copper–chlorine binding giving rise to asymmetrical charge distribution and hence to polarization. The increase in polarization energy may stabilize this structure. A rough qualitative MO picture of the copper–chlorine bonding in this compound seems to indicate that such polarization effects can indeed lower the energy.

Recently the structure determinations of $CsCrCl_3$ (McPherson, Kistenmacher, Folkers & Stucky, 1972) and of $CsCrBr_3$ (Li & Stucky, 1973) have been published. It is interesting to compare the results of these structure determinations with ours. It is stated in both cases that the most probable space group at room temperature is $P6_3mc$ in agreement with our findings in $CsCuCl_3$ at 466°K. The Cr–Cl distances are 2·419 (5) and 2·618 (6) Å in $CsCrCl_3$ and 2·574 (12) and 2·780 (13) Å in $CsCrBr_3$. It is remarkable that three $CsMCl_3$ compounds with M a Jahn–Teller active ion exhibit this particular structure. In $CsCrCl_3$ and $CsCrBr_3$ Stucky and his coworkers found a great deal of anisotropic motion along the c axis which they think arises from a Jahn–Teller effect. In Table 6 we give the root-mean-square amplitudes of vibration along the principal axes and it can be seen (Fig. 1), that in our case too there is some anisotropy in thermal motion along the c axis for the chlorine ion. The similarity in behaviour of these three compounds should in our

Table 6. *Root-mean-square amplitudes of vibration along the principal axes*

Direction cosines are with respect to an orthogonal axis system: $x\perp\mathbf{b}$, $y\parallel\mathbf{b}$, $z\parallel\mathbf{c}$

	$(\overline{u^2})^{1/2}$ (Å)	cosines			$(\overline{u^2})^{1/2}$	cosines			$(\overline{u^2})^{1/2}$	cosines		
Cs	0·30	0	0	1	0·23	1	0	0	0·23	0	1	0
Cu	0·21	0	0	1	0·25	1	0	0	0·25	0	1	0
Cl	0·35	0·17	0·29	0·94	0·23	0·87	−0·50	0	0·25	0·47	0·82	−0·33

opinion clearly be ascribed to the Cu^{2+} and Cr^{2+} ions: both have an orbitally degenerate ground state and can be Jahn–Teller active.

Having seen the close resemblance in behaviour between $CsCuCl_3$ and $CsCrCl_3$ and $CsCrBr_3$ one might wonder if the latter two compounds exhibit a phase transition to a structure with space group $P6_122$ (room-temperature space group of $CsCuCl_3$) at a temperature below 293°K. As far as we know no such behaviour has been reported in the literature.

At present we are preparing a publication on the connexion between the low-temperature structure of $CsCuCl_3$ and the structure with space group $P6_3/mmc$. Natarajan & Prakash (1971) state in an article on phase transitions in ABX_3 type halides that the structure of $CsCuCl_3$ changes from hexagonal to cubic at the transition point. Our calculations, as reported here, prove this statement wrong.

We thank Mrs J. C. M. Tindemans-van Eyndhoven for assistance in the experimental part of the investigation. The investigations were supported in part by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

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Acta Cryst. (1974). B**30**, 1056

Structure Cristalline et Moléculaire du 2-*S*-Ethyl-2-thio-D-mannose Diéthyl Dithioacétal

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(*Reçu le* 16 *novembre* 1973, *accepté le* 12 *décembre* 1973)

The crystal structure of 2-*S*-ethyl-2-thio-D-mannose diethyl dithioacetal ($C_{12}H_{26}O_4S_3$) has been determined by three-dimensional X-ray analysis. The crystals are monoclinic, $a=15\cdot733$, $b=7\cdot214$, $c=16\cdot885$ Å, $\beta=113\cdot23°$ and $Z=4$, space group $P2_1$. The intensities were measured with a four-circle diffractometer using Mo $K\alpha$ radiation. The structure was solved by a modification of the symbolic addition procedure, based on the introduction of the phase function. The stereochemistry at C(2) is *manno* and the sulphur atoms present very short intramolecular contacts. The carbon chain adopts the extended planar zigzag.

Introduction

Les travaux de Horton et collaborateurs (Horton & Miller, 1965; Horton & Wander, 1969) sur les conformations de sucres acycliques par RMN ont mis en évidence leur conformation plane en zigzag lorsqu'il n'existe pas d'interactions stériques entre les substituants portés par des carbones en position alternée. Cette hypothèse a été confirmée dans le cas d'une série d'alditols, par une étude aux rayons X (Jeffrey & Kim,