average Mn–O bond length of 1·61 ± 0·01 Å. The e.s.d. is here set at a somewhat higher value to allow for the effect of some possible systematic errors. This bond length is in close agreement with the result of 1·629 Å found in $KMnO_4$ by Palenik after applying a correction of 0·022 Å for anisotropic motion. Such a correction cannot be made in the present study on account of the incomplete thermal motion data.

The structure as seen in the [001] projection seems to consist of stacks of MnO_4 tetrahedra and rows of Ag atoms extending in the **c** direction. The difference in z coordinates of the Ag and Mn atoms closest in projection is almost exactly $\frac{1}{2}$, and leads to a regular zigzag Ag–Mn–Ag–Mn chain running in the **c** direction. This description probably has no significance since there are closer Ag–Mn (and Ag–O) approaches in other directions. Each Ag atom is in fact surrounded by seven MnO_4 groups with Ag–Mn distances varying between 3·51 and 3·81 Å, and corresponding close Ag–O approaches between 2·33 and 2·67 Å. The shortest Ag–Ag and Mn–Mn distances are 3·63 and 4·33 Å respectively, while the closest approaches between oxygen atoms in different permanganate groups vary from 2·81 to 3·06 Å. The shortest Ag–O and non-bonded O–O distances are markedly shorter than the corresponding distances in $KMnO_4$ (2·62 and 3·06 Å respectively). The present structure is clearly more compact since the molecular volume of $AgMnO_4$ is about 15% smaller than that of $KMnO_4$. The closer approaches found in $AgMnO_4$ compared to $KMnO_4$ can probably be attributed to the fact that $AgMnO_4$ is not a truly ionic compound, but contains a measure of covalent bonding. Unfortunately, accurate data for similar permanganates are not available.

The investigation of the structural aspects of the thermal decomposition of silver permanganate, which led to this structure determination, was undertaken at the suggestion, and under the initial guidance of Dr F.H. Herbstein. In the present work, helpful discussions with Dr G. Gafner are gratefully acknowledged.

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The Crystal Structure of Cd_3As_2

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A Weissenberg study of the structure of Cd_3As_2 has shown that the unit cell is tetragonal ($a = 12·67 \pm 0·01$ Å, $c = 25·48 \pm 0·02$ Å, $Z = 32$, space group $I4_1cd$). Arsenic ions are approximately cubic close-packed and Cd ions are tetrahedrally coordinated. The main difference between the present structure and that proposed by von Stackelberg & Paulus lies in the disposition of the vacant tetrahedral sites. Both structures are geometrically related to the fluorite structure.

Introduction

The crystal structure of Cd_3As_2 was determined by von Stackelberg & Paulus (1935) as tetragonal ($a = 8·95$, $c = 12·65$ Å, space group $P4_2/nmc$) with As ions approximately in a cubic close-packed array. Cd ions were tetrahedrally coordinated and each As ion was surrounded by Cd ions at six of the eight corners of a distorted cube, the two vacant sites being at diagonally opposite corners of a cube face.

In the same paper von Stackelberg & Paulus also reported the crystal structure of Zn_3As_2 as being the same as that of Cd_3As_2, but with somewhat smaller cell parameters. However, a single-crystal study of Zn_3As_2 by Cole, Chambers & Dunn (1956), using rotation and precession techniques, revealed a unit cell which was body-centred tetragonal, the probable space group being $I4_1/acd$ with the a and c parameters, respectively, $\sqrt{2}$ and 2 times those found by von Stackelberg & Paulus.

Two specimens of Cd_3As_2 have been examined in the present work. The first was supplied by Dr D. W. G. Ballentyne, who suggested that the authors might care to re-examine the crystal structure of this material. The second was prepared by Mr G. L. Bucknell of this department as follows: Stoichiometric quantities of cadmium and arsenic were heated in a sealed evacuated silica tube at 675 °C for 18 hours. The sample was then heated at 850 °C for 2 hours prior to air quenching. The resulting polycrystalline mass was found to contain several single crystals sufficiently large for study by the Weissenberg technique. Both specimens were found to give identical X-ray powder patterns, and the powder data given in Table 1 are based on measurements of the patterns of both samples.

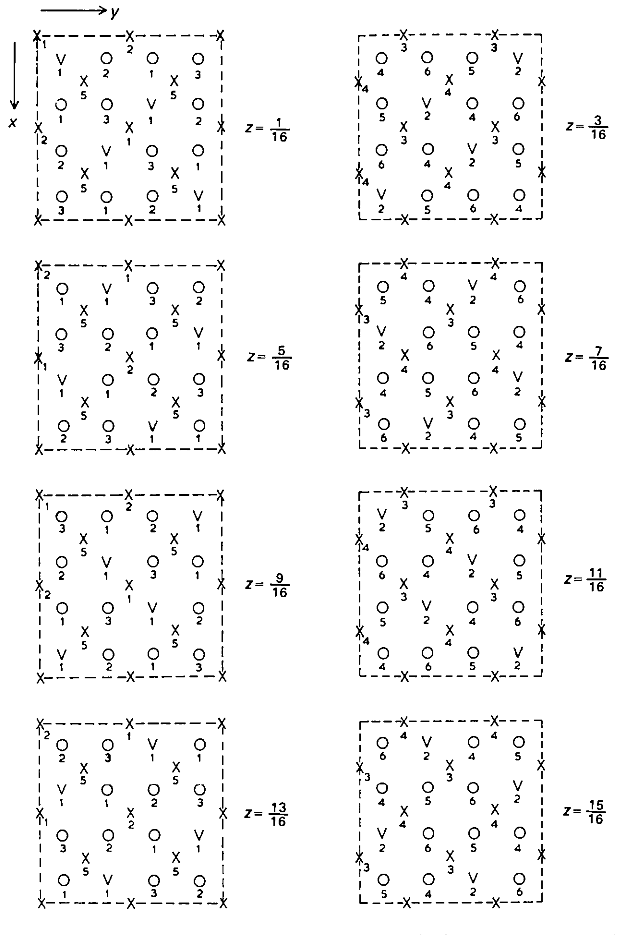

Fig. 1. Idealized structure of Cd_3As_2. Circles represent Cd atoms in the plane of the diagram. Crosses represent As atoms at $\Delta z=\frac{1}{16}$ below the plane of the diagram. $V1$ and $V2$ are vacant Cd sites in first and second sets, respectively, of equivalent positions.

Table 1. *Observed and calculated powder data*

In the Table $I_c \propto |F_c|^2 p f_1(\theta)$, where p is the multiplicity and $f_1(\theta)$ is the angular term defined by Goodyear & Duffin (1957). No correction has been made for absorption since this is nearly constant for all reflexions.

For the observed powder reflexions the reliability index

$$\Sigma\, ||\sqrt{I_o}| - |\sqrt{I_c}|| / \Sigma\, |\sqrt{I_o}| = 0{\cdot}090$$

	d_o	d_c	hkl	I_c	ΣI_c	I_o
	7·35 Å	7·33 Å	112	49	49	57
	5·55	5·54	121	48	48	43
	4·72	4·71	123	127	127	94
	3·831	3·837	116	137	362	465
		3·822	132	225		
	3·785	3·790	125	206	206	149
	3·664	3·664	224	933	933	1114
	3·482	3·482	231	66	66	41
	3·248	3·247	233	317	317	297
	3·186	3·185	008	169	516	586
	3·167	3·167	040	347		
	3·063	3·063	127	44	44	36
	2·914	2·915	136	278	361	316
		2·908	332	83		
	2·892	2·893	235	7	493	414
		2·889	143	486		
	2·527	2·528	237	70	70	40
	2·442	2·443	336	131	148	130
		2·439	152	17		
	2·242	2·246	048	1824	2734	2847
		2·240	440	910		
	2·141	2·144	12,11	9	39	29
		2·144	156	18		
		2·142	352	12		
	1·932	1·934	356	39	500	537
		1·934	23,11	14		
		1·928	165	28		
		1·927	453	5		
(vb)	1·912	1·919	22,12	142		
		1·911	264	272		
	1·853	1·852	12,13	49	161	130
	1·842	1·845	455	4		
		1·844	363	47		
	1·831	1·832	448	61		
(vb)	1·776	1·784	11,14	46	161	115
		1·779	15,10	24		
		1·774	552	11		
			172	42		
		1·771	365	38		
(vb)	1·707	1·712	23,13	75	200	175
		1·705	273	125		
	1·656	1·657	13,14	83	283	306
		1·651	176	68		
			556	1		
	1·647	1·647	275	131		
	1·593	1·593	00,16	107	323	221
	1·583	1·584	080	216		

Since von Stackelberg and Paulus employed a rather different method of preparation (hydrogen and nitrogen gas transfer techniques) there is a small possibility that the disagreement between their structural data and those reported here is due to a difference in crystal structure rather than in quality of X-ray technique.

Weissenberg photographs of a suitable single crystal indicated a body-centred tetragonal cell approximately four times the size of the cell found by von Stackelberg & Paulus. An accurate determination of the lattice parameters, obtained from powder data, taken with Cu *Kα* radiation and a crystal-focusing camera of effective diameter 22·9 cm, gave $a = 12{\cdot}67 \pm 0{\cdot}01$ and $c = 25{\cdot}48 \pm 0{\cdot}02$ Å. This suggests the same relation to the data of von Stackelberg and Paulus as was found by Cole *et al.* for Zn_3As_2. Calculated and observed lattice spacings are compared in Table 1.

Intensity measurements

The crystal selected for measuring intensities was of approximately square cross-section, of side 0·003 cm, and was elongated parallel to [110]. Sixteen layer lines were recorded on equi-inclination Weissenberg photographs taken about [110] with Cu *Kα* radiation.

Systematically absent reflexions were those for which $h+k+l=2n+1$, $2h+1=4n+1$ for hhl, $l=2n+1$ for $0kl$ and possibly $h=2n+1$ for $hk0$. These suggest $I4_1cd$ or $I4_1/acd$ as the space group.

The cell and possible space groups permit more than 2000 reflexions within one octant of the sphere of reflexion for Cu *Kα* radiation. However, about 65% of these proved too weak to be recorded. Hence the intensities of 713 recorded reflexions were estimated visually from multiple film exposures using a calibrated scale. The observed intensities were corrected for Lorentz and polarization factors and were adjusted for spot shape on the upper layer lines (Phillips, 1954). Absorption corrections were made by assuming the crystal to be cylindrical, mean $\mu r = 3{\cdot}4$, and applying the correction factors given by Bond (1959).

The intensities of the powder reflexions, given in Table 1 were obtained from a microdensitometer trace.

The determination of the structure

From a consideration of the cell size and diameter, 4·44 Å (Clark, 1955), of the large As ion it follows that the As ions must be cubic close-packed, or very nearly so. For one face-centred cube of As ions, the cube side would be 6·3 Å; this is about one half of the *a* parameter (12·67 Å) and one quarter of the *c* parameter (25·48 Å) of the unit cell. It would appear then that the cell contains 16 such cubes, *i.e.* 64 As ions. With 32 formula units per cell the X-ray density is 6·31 g.cm^{-3}, which is in reasonable agreement with the observed macroscopic density of 6·21 g.cm^{-3} (*Handbook of Chemistry and Physics*, 1961). With the Cd ions in tetrahedral coordination, it is possible to arrange them around each As ion as in the structure of von Stackelberg & Paulus to give a structure consistent with the symmetry of the space group $I4_1cd$, the essential difference between the two structures being the orientation of the vacant cadmium sites. This distribution of Cd ions was not permitted in the other suggested space group, $I4_1/acd$.

The ideal parameters of the proposed structure are given in column (i) of Table 2. Initial intensity calculations, using atomic scattering factors for the neutral atoms as listed in *International Tables for X-ray*

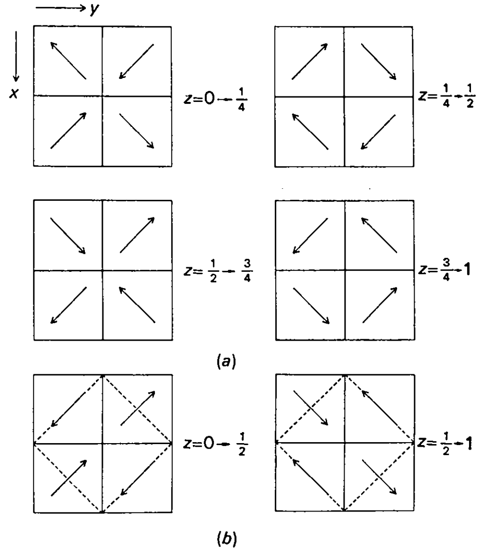

Fig. 2. Relation of the fluorite structure to (*a*) the present structure of Cd_3As_2 and (*b*) the structure proposed by von Stackelberg & Paulus. In (*b*) the broken line indicates the base of the unit cell.

Table 2. *Atomic parameters*

(Origin on 2). Standard deviations are given in brackets.

		(i) Initial			(ii) Final			
Atom	Equipoint	*x*	*y*	*z*	*x*	*y*	*z*	*B*
Cd(1)	16(*b*)	$\frac{3}{8}$	$\frac{1}{8}$	$\frac{1}{16}$	0·3554 (11)	0·1208 (10)	0·0618 (05)	2·95 (21) Å^2
Cd(2)	16(*b*)	$\frac{1}{8}$	$\frac{3}{8}$	$\frac{1}{16}$	0·1188 (09)	0·3584 (09)	0·0528 (04)	2·54 (19)
Cd(3)	16(*b*)	$\frac{3}{8}$	$\frac{3}{8}$	$\frac{1}{16}$	0·3933 (10)	0·3933 (11)	0·0727 (04)	2·18 (14)
Cd(4)	16(*b*)	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{3}{16}$	0·1088 (11)	0·1059 (11)	0·1772 (04)	2·35 (15)
Cd(5)	16(*b*)	$\frac{3}{8}$	$\frac{1}{8}$	$\frac{3}{16}$	0·3799 (10)	0·1458 (10)	0·1892 (05)	2·86 (20)
Cd(6)	16(*b*)	$\frac{1}{8}$	$\frac{3}{8}$	$\frac{3}{16}$	0·1417 (09)	0·3797 (08)	0·1966 (04)	2·24 (17)
As(1)	8(*a*)	0	0	0	0	0	0·0001 (06)	1·42 (36)
As(2)	8(*a*)	0	0	$\frac{1}{4}$	0	0	0·2497 (06)	1·52 (37)
As(3)	16(*b*)	0	$\frac{1}{4}$	$\frac{1}{8}$	0·0072 (15)	0·2540 (11)	0·1231 (10)	2·18 (35)
As(4)	16(*b*)	$\frac{1}{4}$	0	$\frac{1}{8}$	0·2542 (10)	−0·0055 (13)	0·1259 (10)	1·85 (32)
As(5)	16(*b*)	$\frac{1}{4}$	$\frac{1}{4}$	0	0·2588 (10)	0·2399 (19)	−0·0005 (12)	1·41 (21)

Crystallography (1962) and assuming an overall temperature factor of 0·47 Å², gave a reliability index, $R=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$, of about 60%. However, an inspection of the observed and calculated structure factors of the 00*l* reflexions suggested that the Cd ions situated next to a vacant Cd site should be moved about 0·25 Å towards the vacant site. When each Cd ion was moved 0·25 Å towards neighbouring vacant sites, *R* decreased to about 30%. At this stage a three-dimensional least-squares refinement with isotropic

Table 3. *Observed and calculated structure factors*

The 440 and 048 single-crystal reflexions probably suffer from extinction; for these reflexions the agreement between the observed and calculated powder intensities is quite satisfactory.

H	K	L	F_o	F_c	α_c
0	0	8	1838	1723	182
0	0	16	2087	2841	0
0	0	32	488	434	3
0	2	12	237	211	0
0	2	14	171	155	0
0	4	0	1967	1768	180
0	4	8	2570	4143	0
0	4	16	465	385	190
0	4	24	1105	1113	0
0	6	0	219	176	180
0	6	4	255	238	353
0	6	8	130	132	1
0	6	12	397	439	176
0	6	20	331	444	359
0	6	22	164	245	359
0	6	28	198	262	178
0	8	0	2080	2856	0
0	8	8	660	465	183
0	8	16	1403	1551	0
0	8	24	202	250	347
0	10	0	264	250	0
0	10	12	403	477	358
0	10	14	238	210	0
0	10	20	346	401	177
0	10	24	98	100	6
0	10	26	68	34	170
0	12	8	1200	1133	0
0	14	0	209	152	180
0	14	4	175	179	353
0	14	8	184	174	0
0	14	12	202	230	176
0	14	14	112	84	194
0	16	0	475	443	0
1	1	6	849	639	270
1	1	10	361	276	268
1	1	14	800	806	90
1	1	18	317	320	87
1	1	22	531	602	270
1	1	26	202	214	266
1	1	30	343	375	90
1	2	1	251	170	259
1	2	3	373	333	94
1	2	5	661	568	92
1	2	7	362	338	268
1	2	11	274	212	95
1	2	13	547	578	266
1	2	15	339	386	96
1	2	19	289	343	266
1	2	21	238	262	89
1	2	23	228	307	269
1	2	27	241	348	90
1	2	31	163	203	93
1	3	2	674	580	90
1	3	6	883	862	90
1	3	14	779	829	270
1	3	22	460	558	90
1	3	30	294	301	273
1	4	1	247	187	72
1	4	3	186	137	301
1	4	5	146	72	305
1	4	7	149	174	278
1	4	9	178	168	282
1	4	11	142	137	72
1	4	17	280	323	83
1	5	2	290	262	269
1	5	6	409	300	91
1	5	10	472	415	90
1	5	14	484	459	269
1	5	18	439	433	269
1	5	22	433	511	89
1	5	26	201	208	89
1	5	30	249	298	270
1	6	5	523	422	259
1	6	7	162	178	116
1	6	13	260	228	96
1	6	15	219	225	260
1	6	19	314	372	94
1	6	21	236	255	257
1	6	23	215	230	100
1	6	27	194	225	263
1	7	2	605	572	271
1	7	6	764	771	271
1	7	10	440	372	91
1	7	14	514	559	90
1	7	22	380	374	273
1	8	3	196	148	65
1	8	9	436	417	80
1	8	11	259	202	291
1	8	15	290	293	275
1	8	17	279	270	279
1	8	19	131	154	72
1	8	25	252	330	83
1	9	2	268	215	92
1	9	10	458	446	269
1	9	14	292	267	89
1	9	18	292	234	91
1	9	22	292	234	269
1	9	26	184	186	270
1	10	11	304	312	98
1	10	13	247	202	244
1	11	2	408	518	89
1	11	6	372	406	90
1	11	10	294	293	274
1	11	14	305	340	274
1	11	18	216	189	93
1	11	22	109	117	94
1	12	1	202	191	66
1	12	3	199	142	305
1	12	7	190	219	281
1	12	9	131	129	291
1	12	11	125	139	66
1	12	17	279	367	80
1	12	19	133	158	289
1	13	2	214	233	269
1	13	10	227	178	92
1	13	18	219	202	269
1	14	3	235	267	98
1	14	7	99	88	225
1	14	9	91	119	119
1	15	2	210	233	272
1	15	6	217	255	274
1	15	10	240	270	89
2	2	4	1831	1735	0
2	2	12	1315	1356	358
2	2	20	697	836	357
2	2	28	572	567	356
2	3	1	426	345	5
2	3	3	944	816	359
2	3	5	1339	1155	178
2	3	7	552	504	185
2	3	9	177	115	175
2	3	11	252	303	184
2	3	13	679	781	0
2	3	15	410	458	1
2	3	19	130	157	179
2	3	21	312	410	177
2	3	23	255	328	186
2	3	27	164	235	354
2	3	31	119	169	1
2	4	12	172	166	174
2	5	3	331	290	5
2	5	5	176	78	344
2	5	11	441	403	178
2	5	13	234	139	181
2	5	15	155	144	175
2	5	19	373	448	0
2	5	21	202	169	349
2	5	23	187	182	3
2	5	27	242	281	177
2	6	4	1371	1324	359
2	6	12	1056	932	359
2	6	20	814	810	357
2	6	28	386	410	356
2	7	1	385	359	176
2	7	3	938	1008	181
2	7	5	1133	1066	1
2	7	7	436	423	0
2	7	9	223	190	6
2	7	11	460	495	359
2	7	13	746	812	179
2	7	15	298	360	186
2	7	21	295	353	3
2	7	23	229	210	3
2	7	29	70	90	183
2	9	3	333	344	179
2	9	5	222	241	356
2	9	11	428	426	1
2	9	19	277	291	177
2	10	4	730	770	0
2	10	12	805	780	358
2	10	20	423	410	357
2	11	1	257	274	1
2	11	3	662	735	359
2	11	5	775	794	180
2	11	7	269	270	185
2	11	9	243	204	175
2	11	11	503	500	181
2	11	13	527	541	2
2	11	15	205	179	1
2	11	17	129	107	1
2	11	19	174	174	2
2	11	21	259	270	182
2	11	23	87	90	193
2	13	3	291	291	1
2	13	5	170	197	182
2	13	7	163	179	174
2	13	11	243	227	177
2	14	4	542	497	359
2	14	12	358	346	359
2	15	1	242	175	175
2	15	3	461	442	179
2	15	5	441	416	3
2	15	7	157	125	1
2	15	9	188	167	358
2	15	11	247	311	359
3	3	2	898	666	270
3	3	6	1125	1012	269
3	3	10	467	343	95
3	3	14	746	785	91
3	3	18	136	46	54
3	3	22	510	549	270
3	3	30	244	253	94
3	4	9	393	325	262
3	4	15	256	260	92
3	4	17	259	245	97
3	4	25	211	268	265
3	5	2	313	247	274
3	5	6	648	499	273
3	5	14	619	592	88
3	5	18	199	167	80
3	5	22	473	428	272
3	5	26	124	139	268
3	5	30	232	260	89
3	6	1	182	165	64
3	6	3	601	576	277
3	6	5	545	542	273
3	6	7	260	257	80
3	6	13	592	594	83
3	6	15	262	301	283
3	6	21	196	199	277
3	6	23	191	201	85
3	6	27	172	226	273
3	7	2	647	689	93
3	7	6	667	655	92
3	7	10	366	267	272
3	7	14	540	638	269
3	7	18	183	139	106
3	7	22	300	328	94
3	8	1	252	182	245
3	8	7	318	322	96
3	8	9	235	203	103
3	8	11	162	112	233
3	8	13	160	90	136
3	8	15	298	207	253
3	8	17	472	482	263
3	8	23	177	261	94
3	8	25	199	265	97
3	9	6	304	258	85
3	9	14	325	273	274
3	9	18	219	168	274
3	9	22	309	279	86
3	10	5	348	313	73
3	10	19	247	172	281
3	10	21	203	177	70
3	11	2	308	330	268
3	11	6	426	472	268
3	11	10	314	319	96
3	11	14	246	265	95
3	11	18	132	58	279
3	11	22	190	199	270
3	12	9	369	341	258
3	12	15	268	327	96
3	12	17	212	233	100
3	13	14	161	157	82
3	13	18	74	61	72
3	15	2	226	249	95
3	15	6	136	139	97
3	15	10	146	110	268
4	4	0	2718	4141	0
4	4	8	1215	928	182
4	4	16	1700	2079	0
4	5	3	250	178	351
4	5	5	253	158	157
4	5	7	150	79	213
4	5	9	258	231	170
4	5	11	222	175	197
4	6	12	340	407	358
4	6	14	233	203	0
4	6	20	284	352	177
4	6	28	185	242	1
4	7	7	227	202	3
4	7	17	276	289	355
4	7	25	132	173	187
4	8	0	578	476	180
4	8	8	1750	2081	0
4	8	16	246	44	287
4	8	24	702	697	0
4	9	1	133	131	168
4	9	3	190	185	195
4	9	5	133	160	6
4	10	4	209	211	353
4	10	12	310	332	176
4	10	20	328	399	359
4	10	22	136	206	357
4	10	24	92	63	180
4	12	0	1059	1117	0
4	12	16	809	700	359
4	14	0	163	167	0
4	14	12	228	291	357
5	5	2	607	421	94
5	5	6	268	160	99
5	5	10	742	700	268
5	5	14	320	326	92
5	5	18	436	441	93
5	5	22	348	320	267
5	5	26	277	258	269
5	6	11	455	459	94
5	6	13	266	176	249
5	6	19	276	301	263
5	6	27	262	281	93
5	7	2	468	460	85
5	7	6	560	519	67
5	7	10	259	225	280
5	7	14	408	446	275
5	7	22	257	263	87
5	8	1	271	229	73
5	8	3	268	260	290
5	8	5	210	188	283
5	8	7	132	95	291
5	8	11	205	203	79
5	8	17	221	293	80
5	8	19	145	169	288
5	8	23	108	120	278
5	9	2	545	553	267
5	9	6	254	154	259
5	9	10	470	471	95
5	9	18	444	417	268
5	9	22	214	225	92
5	10	3	310	343	97
5	10	11	209	204	254
5	10	21	226	119	240
5	11	2	372	381	274
5	11	6	433	397	277
5	11	10	343	334	85
5	11	14	236	211	86
5	12	3	205	183	77
5	12	5	163	174	64
5	12	9	261	260	76
5	12	11	223	205	290
5	12	13	91	92	299
5	12	15	139	139	282
5	13	2	288	250	98
5	13	6	272	249	96
5	13	10	370	349	267
5	14	1	122	119	115
5	14	5	181	216	262
5	14	11	207	277	97
5	15	2	252	290	82
5	15	6	134	168	84
6	6	4	967	906	0
6	6	12	1122	1059	358
6	6	20	357	385	357
6	7	1	206	193	12
6	7	3	627	564	357
6	7	5	805	779	176
6	7	7	265	263	194
6	7	11	389	400	186
6	7	13	399	464	3
6	7	15	240	202	355
6	7	21	276	293	174
6	7	23	144	153	196
6	8	12	165	199	174
6	8	16	160	107	8
6	8	18	237	16	3
6	8	20	172	247	359
6	9	3	390	378	5
6	9	11	290	280	173
6	9	19	277	304	2
6	10	4	865	767	359
6	10	12	340	345	0
6	10	20	793	663	358
6	11	1	199	181	167
6	11	3	627	568	183
6	11	5	503	499	3
6	11	11	342	318	357
6	11	13	447	417	178
6	11	21	88	153	11
6	12	3	162	182	3
6	13	1	116	120	197
6	13	3	187	175	173
6	13	5	181	204	355
6	13	7	87	127	8
6	13	11	228	235	3
6	14	4	352	336	1
6	15	1	116	116	4
6	15	3	238	299	356
7	7	2	414	361	267
7	7	6	581	590	266
7	7	10	327	313	100
7	7	14	368	383	95
7	7	22	322	305	268
7	8	9	329	324	261
7	8	15	247	322	92
7	8	17	215	264	98
7	9	2	283	258	279
7	9	6	327	292	280
7	9	14	342	263	83
7	9	16	134	130	273
7	9	22	181	155	282
7	10	3	352	333	281
7	10	5	231	198	278
7	10	13	330	283	78
7	11	2	293	300	101
7	11	6	229	221	98
7	11	10	105	68	257
7	11	14	334	287	263
7	11	18	145	88	120
7	12	7	230	263	96
7	12	15	78	156	252
7	13	6	214	164	76
7	14	1	89	68	55
7	14	5	114	105	53
8	8	0	1186	1523	0
8	8	16	1179	908	0
8	9	3	234	232	355
8	9	5	257	233	165
8	9	7	160	147	197
8	9	9	110	177	167
8	9	11	178	204	197
8	10	12	204	267	357
8	11	7	182	193	3
8	11	17	182	258	355
8	12	8	761	669	0
8	13	1	149	120	169
8	13	3	160	187	194
8	13	5	139	175	5
9	9	2	579	397	98
9	9	6	510	362	96
9	9	10	584	505	267
9	9	18	314	262	100
9	10	5	191	215	262
9	10	11	292	309	95
9	11	2	287	278	78
9	11	6	269	231	81
9	11	10	191	207	283
9	11	14	193	153	289
9	12	1	190	160	73
9	12	3	211	222	287
9	12	5	166	178	279
9	12	11	128	145	82
9	13	2	393	353	265
9	13	6	241	189	256
10	10	4	413	370	2
10	10	12	731	654	358
10	11	3	250	201	353
10	11	5	361	295	173
10	11	9	244	63	141
10	12	0	190	192	0
10	12	8	108	84	185
11	11	6	209	191	253

temperature factors was carried out on an Elliott 803B computer. After several cycles of refinement the value of R decreased to 15·9% at which stage changes in atomic parameters became less than the standard deviations.

The final atomic parameters are listed in column (ii) of Table 2 and observed and calculated structure factors are compared in Table 3, the mean value of $|F_o|$ for *hkl* and *khl* reflexions being given (R = 14·6%). Of the possible reflexions which were too weak to be recorded $|F_c|$ was found in each case to be less than the lowest observable $|F_o|$ and these data have not been used in the calculation of R and are not included in Table 3. Calculated intensities of powder reflexions are given in Table 1.

Discussion of the structure

The ideal structure is illustrated in Fig. 1, which shows successive layers of atoms parallel to the (001) face of the unit cell. The main shifts from idealized positions occur with the cadmium ions; each such ion is displaced about 0·20 Å or 0·25 Å towards neighbouring Cd vacancies. Other components of displacement are much smaller, being 0·05 Å.

The arsenic ions are but slightly displaced, relatively speaking, particularly As(1) and As(2) which lie on the twofold axes of the space group. As(5) ions almost lie on the fourfold screw axes and show the largest shifts; during the refinement process the parameters of As(5) ions were less inclined to converge to definite

Table 4. *Bond lengths*

Standard deviations are given in brackets.

Cd(1)–As tetrahedron	Cd–As(2)	2·87 (2) Å	As(2)–As(4)	4·49 (2) Å
	Cd–As(3)	2·95 (2)	As(2)–As(3)	4·44 (2)
	Cd–As(4)	2·62 (2)	As(2)–As(5)	4·32 (3)
	Cd–As(5)	2·51 (3)	As(3)–As(4)	4·53 (3)
			As(3)–As(5)	4·46 (3)
			As(4)–As(5)	4·49 (3)
Cd(2)–As tetrahedron	Cd–As(2)	2·71 (1)	As(2)–As(3)	4·44 (2)
	Cd–As(3)	2·65 (2)	As(2)–As(4)	4·49 (2)
	Cd–As(4)	3·01 (2)	As(2)–As(5)	4·66 (3)
	Cd–As(5)	2·70 (3)	As(3)–As(4)	4·30 (3)
			As(3)–As(5)	4·50 (3)
			As(4)–As(5)	4·57 (3)
Cd(3)–As tetrahedron	Cd–As(1)	2·67 (1)	As(1)–As(3)	4·51 (2)
	Cd–As(3)	2·69 (2)	As(1)–As(4)	4·56 (2)
	Cd–As(4)	2·65 (2)	As(1)–As(5)	4·50 (3)
	Cd–As(5)	3·20 (3)	As(3)–As(4)	4·58 (3)
			As(3)–As(5)	4·47 (3)
			As(4)–As(5)	4·58 (3)
Cd(4)–As tetrahedron	Cd–As(2)	2·68 (2)	As(2)–As(3)	4·57 (2)
	Cd–As(3)	2·67 (2)	As(2)–As(4)	4·53 (2)
	Cd–As(4)	2·67 (2)	As(2)–As(5)	4·32 (3)
	Cd–As(5)	3·02 (3)	As(3)–As(4)	4·55 (3)
			As(3)–As(5)	4·39 (3)
			As(4)–As(5)	4·46 (3)
Cd(5)–As tetrahedron	Cd–As(1)	2·86 (2)	As(1)–As(3)	4·51 (2)
	Cd–As(3)	2·66 (2)	As(1)–As(4)	4·46 (2)
	Cd–As(4)	2·98 (2)	As(1)–As(5)	4·50 (3)
	Cd–As(5)	2·65 (3)	As(3)–As(4)	4·53 (3)
			As(3)–As(5)	4·69 (3)
			As(4)–As(5)	4·46 (3)
Cd(6)–As tetrahedron	Cd–As(1)	2·73 (1)	As(1)–As(3)	4·51 (2)
	Cd–As(3)	3·00 (2)	As(1)–As(4)	4·46 (2)
	Cd–As(4)	2·67 (2)	As(1)–As(5)	4·48 (3)
	Cd–As(5)	2·55 (3)	As(3)–As(4)	4·30 (3)
			As(3)–As(5)	4·39 (3)
			As(4)–As(5)	4·51 (3)
Vacant tetrahedra	As(1)–As(3)	4·51 (2)	As(2)–As(3)	4·57 (2)
	As(1)–As(4)	4·56 (2)	As(2)–As(4)	4·52 (2)
	As(1)–As(5)	4·48 (3)	As(2)–As(5)	4·66 (3)
	As(3)–As(4)	4·55 (3)	As(3)–As(4)	4·57 (3)
	As(3)–As(5)	4·50 (3)	As(3)–As(5)	4·70 (3)
	As(4)–As(5)	4·49 (3)	As(4)–As(5)	4·52 (3)

values than were any of the other atomic parameters.

The present structure and that of von Stackelberg and Paulus are related geometrically to the structure of fluorite; this is illustrated in Fig. 2. Consider one fluorite-type unit cell with As^{3-} replacing Ca^{2+} and Cd^{2+} replacing F^-, but with two cube-diagonally opposite fluorite sites vacant. The unit cell of Goodyear and Steigmann contains 16 such units in the orientation shown in Fig. 2(*a*), the tail and head of the arrow being situated at the upper and lower vacant sites, respectively, in one unit. Fig. 2(*b*) shows the orientation of such units in the structure of Stackelberg and Paulus, there being 4 units in one unit cell of structure.

Cd–As and As–As bond lengths in each type of As tetrahedron are given in Table 4. The variation in some of the As–As distances shows that there is appreciable distortion from cubic close-packing of As ions.

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A Refinement of the Structure of Calcium Hexa-antipyrine Perchlorate and a Comparative Study of Some Metal Hexa-antipyrine Perchlorates

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Calcium hexa-antipyrine perchlorate, $Ca(C_{11}H_{12}ON_2)_6(ClO_4)_2$, is isomorphous with the corresponding magnesium and lead compounds and crystallizes in the trigonal space group $P\bar{3}$ with one formula unit in an elementary cell of dimensions $a = 14{\cdot}33$ and $c = 9{\cdot}78$ Å. The structure was refined by structure-factor least-squares method to an R value of 0·118 for 1131 observed reflexions. The structural features of magnesium, calcium and lead hexa-antipyrine perchlorates are compared. The coordination of antipyrine oxygen atoms around the metal ion is octahedral in all three cases; this octahedron becomes elongated along the $\bar{3}$ axis as the size of the metal ion increases. The nature of the metal–oxygen bonds is discussed on the basis of the known electronegativity coefficients of the relevant atoms and the observed metal–oxygen distances. In the antipyrine molecule, both the phenyl and the pyrazolone rings are planar and are inclined with respect to each other by angles varying from 62 to 68°. An attempt has been made to explain the observed bond lengths in the pyrazolone ring in terms of the major canonical structures proposed.

Introduction

The present study forms part of a program of systematic X-ray investigation of some metal antipyrine compounds undertaken in this laboratory to study the nature of the metal–oxygen bonding in these and also to elucidate the geometry of the antipyrine ring system. Independent analyses of the isostructural lead and magnesium hexa-antipyrine perchlorates have already been reported (Vijayan & Viswamitra, 1966, 1967). Divalent calcium has an ionic radius ($r = 0{\cdot}99$ Å) mid-way between those of Mg^{2+} ($r = 0{\cdot}65$ Å) and Pb^{2+} ($r = 1{\cdot}21$ Å) (Wells, 1962) and hence it was thought worth whiie to analyse the structure of the calcium compound to facilitate a study of the changes introduced in the molecular geometry and packing as a result of the change in the size of the central metal ion. In addition, it would

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