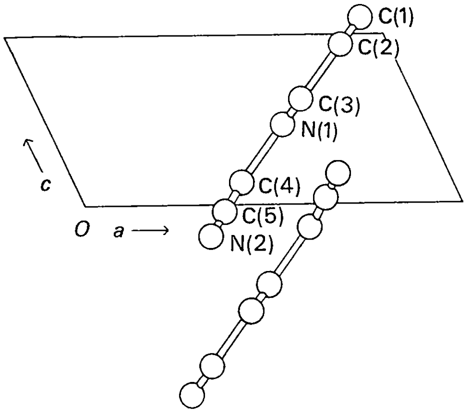

Fig. 2. Projection of the pyridinium dicyanomethylide structure down [010].

distance is 3·37 Å distance between C(3) and N(2) of molecules related by a center of symmetry.

The authors intend to attempt the synthesis and structural determination of *p*-nitropyridinium dicyanomethylide. It is hoped that introduction of the nitro group will offer an opportunity to observe the effect of increased conjugation upon the planarity of the carbanion.

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The Crystal Structure of Ternary Silicides ThM_2Si_2 (M=Cr, Mn, Fe, Co, Ni and Cu)

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The existence of well defined and isomorphous ternary phases of the general composition ThM_2Si_2 (M=Cr, Mn, Fe, Co, Ni and Cu) has been established in the corresponding intermetallic systems. The crystal structure of the isomorphous series of compounds has been determined by the X-ray powder method. The compounds crystallize in the tetragonal system in the space group $I4/mmm$ (D_{4h}^{17}) as determined from the systematically absent reflexions. The unit cells containing two formula units of ThM_2Si_2, have the dimensions: $ThCr_2Si_2$, $a=4{\cdot}043 \pm 0{\cdot}001$, $c=10{\cdot}577 \pm 0{\cdot}002$ Å; $ThMn_2Si_2$, $a=4{\cdot}021 \pm 0{\cdot}001$, $c=10{\cdot}493 \pm 0{\cdot}002$ Å; $ThFe_2Si_2$, $a=4{\cdot}038 \pm 0{\cdot}003$, $c=9{\cdot}820 \pm 0{\cdot}005$ Å; $ThCo_2Si_2$, $a=4{\cdot}015 \pm 0{\cdot}003$, $c=9{\cdot}760 \pm 0{\cdot}005$ Å; $ThNi_2Si_2$, $a=4{\cdot}076 \pm 0{\cdot}001$, $c=9{\cdot}551 \pm 0{\cdot}002$ Å; $ThCu_2Si_2$, $a=4{\cdot}104 \pm 0{\cdot}001$, $c=9{\cdot}864 \pm 0{\cdot}002$ Å.

Introduction

The investigation of the phase relations in the system Th–Mo–Si (Sikirica, 1963) revealed the existence of a compound of the composition close to $ThMo_2Si_2$ with a very complex powder diffraction pattern. The oscillation photographs of a single-crystal fragment showed that the cell is tetragonal with the lattice parameters: $a=4{\cdot}01$ and $c \simeq 87{\cdot}5$ Å. Graphical indexing by means of Bunn charts suggested that a pseudocell, with the parameter c approximately eight times as small, could be chosen for the rough description of the structure. In order to examine the influence of the electronic structure and radii of transition metals upon the formation of such structures, we have investigated the effect of the replacement of molybdenum by chromium, manganese, iron, cobalt, nickel and copper. All of them led to the formation of a new compound of the exact stoichiometric composition ThM_2Si_2. The unit cell in all these cases has almost the same dimen-

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sions as the small pseudocell of the analogous molybdenum compound.

Sample preparation

The following chemicals were used for the preparation of the samples: thorium powder (Nuclearrein Merck thorium), chromium powder (The Coleman & Bell Co.), manganese flake (L. Light & Co. Ltd. 99,9%), iron powder (Chinoin Budapest p. a.), cobalt sponge (Johnson, Matthey), nickel powder (carbonyl nickel, T. Schuchardt & Co 99·8%), copper powder (Merck electrolytic copper) and silicon powder, −200 mesh (Merck silicon powder, spec. resist. 0·1–1 ohm. cm).

All preparations were carried out in a specially designed electron beam furnace (Ban & Sikirica 1962). Powdered mixtures of the components, weighted in the correct proportions, were pressed into rectangular blocks of the dimensions 5 × 5 × 25 mm. A thin molybdenum wire, which would serve for suspending the specimen in an electron beam furnace, was pressed into one end of the compacted mixture. The initiation of the exothermic reaction did not cause melting. The specimen was subjected to a heat treatment until incipient melting occurred, and then slowly cooled. All specimens were then sealed into small quartz tubes filled with purified argon under reduced pressure, and annealed at 1050 °C during 150 hours. This treatment did not significantly alter the relative intensities of the X-ray powder pattern, but improved the resolution of lines, and unfortunately caused oxidation of the specimen (thorium oxide lines were observed).

X-ray procedure

Samples for X-ray studies were generally taken from the most homogeneous parts of specimens. They were easily crushed in an agate mortar under toluene in order to avoid unnecessary oxidation. All X-ray diffraction patterns were obtained by means of a recording Philips diffractometer provided with a Geiger counter tube. Filtered Cu*K* radiation was used throughout the work. Single-crystal photographs were taken with a Unicam camera ($r = 3$ cm). Incoherently scattered radiation caused serious trouble in the determination of lattice parameters of the iron and cobalt compounds. Intensity calculations were carried out only for the compound $ThNi_2Si_2$ which gave the best diffractometer record. The observed intensity values were obtained by measuring the peak heights. Densities were determined pycnometrically only for two representative specimens, viz. $ThMn_2Si_2$ and $ThCu_2Si_2$, by means of redistilled tetrahydronaphthalene.

Crystal structure

X-ray powder patterns of all the compounds were indexed on the basis of a tetragonal unit cell. This has been confirmed by means of the oscillation photographs. Lattice parameters and X-ray densities of all the compounds are given in Table 1. The systematically absent reflexions indicated a body-centered lattice, the space group being $I4/mmm(D_{4h}^{17})$. Density measurements have shown that the unit cell contains two formula units of ThM_2Si_2. From these data it was assumed that the atoms occupy the following positions according to *International Tables for X-ray Crystallography* (1952): 2Th in (*a*), 4M in (*d*) and 4Si in (*e*). This choice has been made because of the well known tendency of silicon atoms towards pairing in silicides. This was actually confirmed by the intensity calculation according to the formula (M = multiplicity factor):

$$I \simeq F^2 M (1 + \cos^2 2\theta)/\sin^2 2\theta \cos\theta .$$

Table 1. *Unit-cell dimensions and densities* of ThM_2Si_2

	a	*c*	D_x	D_m
$ThCr_2Si_2$	4·043 ± 0·001 Å	10·577 ± 0·002 Å	7·53	—
$ThMn_2Si_2$	4·021 ± 0·001	10·493 ± 0·002	7·79	7·67
$ThFe_2Si_2$	4·038 ± 0·003	9·820 ± 0·005	8·29	—
$ThCo_2Si_2$	4·015 ± 0·003	9·760 ± 0·005	8·57	—
$ThNi_2Si_2$	4·076 ± 0·001	9·551 ± 0·002	8·49	—
$ThCu_2Si_2$	4·104 ± 0·001	9·864 ± 0·002	8·30	8·16

The variable parameter z which defines the silicon atom position cannot be evaluated with sufficient accuracy from the intensity data by means of this trial and error procedure. Therefore it was obtained from the Fourier synthesis of electron-density distribution along the *c* axis by using all reflexions recorded. The Fourier series $\varrho(x, y, z)_{\substack{x=0\\y=0}} \simeq \Sigma\, F(hkl) \cos 2\pi lz$, computed by means of Beevers–Lipson strips, gave well resolved maxima for silicon at the values listed in Table 8, except for iron and cobalt compounds because of the difficulties already stated. Careful examination of the relative intensities of the 101 and 103 reflexions suggest that an inadequate heat treatment of specimens may cause partial statistical distribution of the silicon and transition metal atoms over the points 4(*d*) and 4(*e*). Such a distribution of smaller atoms is much more pronounced in the specimens quenched quickly from the melt.

Table 2 presents the diffractometer data for $ThNi_2Si_2$, containing the comparison of the observed and calculated relative intensities together with the observed and calculated $\sin^2\theta$ values. Tables 3–7 list the data for other isomorphous compounds.

Table 2. *Diffractometer data for* $ThNi_2Si_2$

h k l	$\sin^2\theta_o$	$\sin^2\theta_c$	I_o	I_c
0 0 2	0·0261	0·0261	17	16
1 0 1	0·0432	0·0432	160	154
1 1 0	0·0716	0·0715	34	27
1 0 3	0·0945	0·0944	115	113
1 1 2	0·0976	0·0976	200	198
0 0 4	0·1043	0·1041	30	31
2 0 0	0·1430	0·1428	70	75
2 0 2	0·1689	0·1689	11	7·5

Table 2 (*cont.*)

h k l	$\sin^2 \theta_o$	$\sin^2 \theta_c$	I_o	I_c
1 1 4	—	0·1755	—	1·4
2 1 1	0·1853	0·1851	46	42
1 0 5	0·1985	0·1983	40	39
0 0 6	—	0·2341	—	1·1
2 1 3	0·2373	0·2371	65	56
2 0 4	0·2471	0·2469	30	32
2 2 0	0·2855	0·2857	28	24
1 1 6	0·3058	0·3056	33	31
2 2 2	0·3119	0·3117	5·3	3·0
3 0 1	0·3280	0·3279	10	8·2
2 1 5	0·3410	0·3411	33	32
1 0 7	0·3546	0·3544	7·0	7·8
3 1 0	0·3570	0·3571	14	16
2 0 6	—	0·3770	—	1·9
3 0 3	0·3797	0·3799	14	13
3 1 2	0·3829	0·3831	35	35
2 2 4	0·3897	0·3897	14	15
0 0 8	0·4163	0·4163	5·8	6·5
3 1 4	—	0·4612	—	0·8
3 2 1	0·4709	0·4707	9·8	9·7
3 0 5	0·4839	0·4840	9·1	9·7
1 1 8	0·4878	0·4877	7·0	3·7
2 1 7	0·4974	0·4972	9·3	9·8
2 2 6	0·5199	0·5198	5·0	6·0
3 2 3	0·5228	0·5228	15	17
2 0 8	0·5594	0·5591	14	18
1 0 9	—	0·5625	—	3·9
4 0 0	0·5715	0·5714	7·0	4·5
3 1 6	0·5913	0·5913	28	33
4 0 2	—	0·5974	—	1·4
4 1 1	0·6137	0·6136	9·3	7·9
3 2 5	0·6270	0·6268	16	16
3 0 7	—	0·6401	—	4·2
3 3 0	—	0·6428	—	1·5
0 0 10	—	0·6504	—	0·4
4 1 3	0·6654	0·6656	18	15
3 3 2	0·6687	0·6688	12	13
4 0 4	0·6750	0·6754	7·0	9·4
2 2 8	0·7019	0·7019	16	18
2 1 9	0·7058	0·7054	9·3	7·8
4 2 0	0·7141	0·7142	16	18
1 1 10	0·7218	0·7218	12	13
4 2 2	0·7401	0·7402	7·0	3·2
3 3 4	—	0·7469	—	0·5
4 1 5	0·7697	0·7697	18	18

Table 3. *Diffractometer data for* $\mathrm{ThCu_2Si_2}$

h k l	$\sin^2 \theta_o$	$\sin^2 \theta_c$	I_o
0 0 2	0·0244	0·0244	16
1 0 1	0·0413	0·0414	163
1 1 0	0·0705	0·0706	25
1 0 3	0·0901	0·0902	103
1 1 2	0·0948	0·0948	185
0 0 4	0·0976	0·0977	35
2 0 0	0·1409	0·1409	62
2 0 2	0·1654	0·1653	10
1 1 4	—	0·1680	—
2 1 1	0·1824	0·1822	48
1 0 5	0·1877	0·1877	54
0 0 6	—	0·2195	—
2 1 3	0·2311	0·2310	65
2 0 4	0·2385	0·2385	36
2 2 0	0·2816	0·2818	18
1 1 6	0·2898	0·2900	42
2 2 2	0·3061	0·3062	6
3 0 1	0·3229	0·3231	7
2 1 5	0·3285	0·3286	42
1 0 7	0·3339	0·3340	14
3 1 0	0·3521	0·3522	8
2 0 6	0·3605	0·3604	7
3 0 3	0·3719	0·3719	14
3 1 2	0·3767	0·3766	40
2 2 4	0·3904	0·3794	12
0 0 8		0·3903	
3 1 4	—	0·4498	—
1 1 8	0·4605	0·4607	5
3 2 1	0·4639	0·4640	5
3 0 5	0·4693	0·4695	7
2 1 7	0·4749	0·4749	10
2 2 6	—	0·5013	—
3 2 3	0·5127	0·5128	18
1 0 9	—	0·5291	—
2 0 8	0·5314	0·5312	19
4 0 0	0·5635	0·5636	6
3 1 6	0·5718	0·5718	24
4 0 2	—	0·5880	—
4 1 1	0·6050	0·6049	7
0 0 10	0·6104	0·6098	20
3 2 5		0·6104	
3 0 7	0·6157	0·6158	5
3 3 0	—	0·6341	—
4 1 3	0·6537	0·6537	15
3 3 2	0·6585	0·6584	6
4 0 4	0·6615	0·6612	5
2 1 9	—	0·6700	—
2 2 8	0·6720	0·6721	17
1 1 10	0·6803	0·6802	18
4 2 0	0·7045	0·7045	12
4 2 2	—	0·7289	—
3 3 4	—	0·7316	—
3 1 8	0·7424	0·7425	9

Table 4. *Diffractometer data for* $\mathrm{ThCr_2Si_3}$

h k l	$\sin^2 \theta_o$	$\sin^2 \theta_c$	I_o
0 0 2	0·0213	0·0213	52
1 0 1	0·0417	0·0417	120
1 1 0	0·0728	0·0727	38
1 0 3	0·0843	0·0842	150
0 0 4		0·0850	
1 1 2	0·0940	0·0939	180
2 0 0	0·1456	0·1454	58
1 1 4	0·1577	0·1577	6
2 0 2	0·1667	0·1666	10
1 0 5	0·1693	0·1692	60
2 1 1	0·1874	0·1871	34
0 0 6	0·1911	0·1912	4
2 1 3	0·2306	0·2296	76
2 0 4		0·2304	
1 1 6	0·2640	0·2645	48
2 2 0	0·2911	0·2903	2
1 0 7	0·2969	0·2962	10
2 2 2	0·3124	0·3115	6
2 1 5	0·3146	0·3140	46
3 0 1	—	0·3319	—0
2 0 6	—	0·3361	—
0 0 8	0·3394	0·3394	12
3 1 0	0·3627	0·3629	8
3 0 3	0·3756	0·3743	20
2 2 4		0·3752	
3 1 2	0·3845	0·3841	30
1 1 8	0·4125	0·4120	8
2 1 7	0·4416	0·4413	14
3 1 4	—	0·4477	—
3 0 5	0·4599	0·4592	12
1 0 9	0·4655	0·4659	8
3 2 1	0·4773	0·4770	8
2 2 6	—	0·4812	—
2 0 8	0·4848	0·4846	28

Table 4 (*cont.*)

h	*k*	*l*	$\sin^2\theta_o$	$\sin^2\theta_c$	I_o
3	2	3	0·5202	0·5195	10
0	0	10	0·5304	0·5304	4
3	1	6	0·5540	0·5538	22
4	0	0	0·5808	0·5806	6
3	0	7	0·5868	0·5865	6
4	0	2	0·6039	0·6018	22
1	1	10		0·6030	
3	2	5		0·6043	
2	1	9	0·6113	0·6111	8
4	1	1	—	0·6222	—
2	2	8	0·6299	0·6298	18
3	3	0	—	0·6532	—
4	1	3	0·6652	0·6646	12
4	0	4		0·6655	
3	3	2	0·6751	0·6744	10
2	0	10		0·6755	
1	0	11	0·6780	0·6780	10
3	1	8	0·7027	0·7023	10

Table 5. *Diffractometer data for* $ThMn_2Si_2$

h	*k*	*l*	$\sin^2\theta_o$	$\sin^2\theta_c$	I_o
0	0	2	0·0214	0·0216	20
1	0	1	0·0420	0·0422	130
1	1	0	0·0741	0·0735	36
1	0	3	0·0851	0·0853	118
0	0	4		0·0864	
1	1	2	0·0951	0·0951	168
2	0	0	0·1468	0·1470	58
1	1	4	—	0·1596	—
2	0	2	0·1680	0·1683	10
1	0	5	0·1711	0·1714	44
2	1	1	0·1885	0·1889	40
0	0	6	—	0·1940	—
2	1	3	0·2319	0·2320	50
2	0	4	0·2328	0·2330	38
1	1	6	0·2674	0·2674	28
2	2	0	0·2934	0·2936	20
1	0	7	0·3014	0·3007	8
2	2	2	0·3146	0·3151	4
2	1	5	0·3179	0·3182	34
3	0	1	0·3354	0·3357	6
2	0	6	—	0·3408	—
0	0	8	—	0·3449	—
3	1	0	0·3662	0·3670	8
3	0	3	0·3794	0·3788	22
2	2	4		0·3798	
3	1	2	0·3880	0·3885	34
1	1	8	0·4175	0·4183	5
2	1	7	0·4469	0·4475	8
3	1	4	—	0·4532	—
3	0	5	0·4648	0·4650	8
1	0	9	—	0·4732	—
3	2	1	—	0·4825	—
2	2	6	—	0·4876	—
2	0	8	0·4913	0·4917	16
3	2	3	0·5250	0·5256	16
0	0	10	—	0·5389	—
3	1	6	0·5595	0·5610	20
4	0	0	—	0·5872	—
3	0	7	—	0·5943	—
4	0	2	0·6113	0·6087	30
3	2	5		0·6118	
1	1	10		0·6123	
2	1	9	—	0·6200	—
4	1	1	0·6292	0·6293	6
2	2	8	0·6380	0·6385	12
3	3	0	—	0·6606	—
4	1	3	0·6728	0·6724	14
4	0	4		0·6734	
3	3	2	0·6816	0·6821	9

Table 6. *Diffractometer data for* $ThFe_2Si_2$

h	*k*	*l*	$\sin^2\theta_o$	$\sin^2\theta_c$	I_o
0	0	2	0·0249	0·0247	20
1	0	1	0·0428	0·0425	151
1	1	0	0·0730	0·0729	37
1	0	3	0·0922	0·0918	140
1	1	2	0·0978	0·0975	198
0	0	4		0·0984	
2	0	0	0·1459	0·1456	65
2	0	2	0·1713	0·1702	10
1	1	4		0·1712	
2	1	1	0·1885	0·1881	49
1	0	5	0·1907	0·1902	49
0	0	6	—	0·2215	—
2	1	3	0·2377	0·2373	64
2	0	4	0·2443	0·2440	37
2	2	0	0·2915	0·2911	20
1	1	6	0·2947	0·2943	47
2	2	2	—	0·3157	—
3	0	1	0·3361	0·3336	40
2	1	5		0·3357	
1	0	7		0·3379	
3	1	0	—	0·3639	—
2	0	6	—	0·3670	—
3	0	3	0·3829	0·3829	12
3	1	2	0·3892	0·3885	36
2	2	4		0·3895	
0	0	8	0·3935	0·3938	10
3	1	4	—	0·4623	—
1	1	8	—	0·4665	—
3	2	1	0·4791	0·4792	7
3	0	5	0·4813	0·4813	10
2	1	7	0·4830	0·4834	10
2	2	6	0·5115	0·5126	6
3	2	3	0·5282	0·5284	15
1	0	9	0·5349	0·5347	5
2	0	8	0·5396	0·5393	21
4	0	0	—	0·5822	—
3	1	6	0·5854	0·5854	25
4	0	2	—	0·6806	—
0	0	10	—	0·6152	—
4	1	1	—	0·6247	—
3	2	5	0·6269	0·6269	15
3	0	7	—	0·6290	—
3	3	0	—	0·6550	—
4	1	3	0·6735	0·6740	10

Table 7. *Diffractometer data for* $ThCo_2Si_2$

h	*k*	*l*	$\sin^2\theta_o$	$\sin^2\theta_c$	I_o
0	0	2	0·0252	0·0249	24
1	0	1	0·0432	0·0431	148
1	1	0	0·0735	0·0737	36
1	0	3	0·0930	0·0930	130
1	1	2	0·0985	0·0987	200
0	0	4		0·0965	
2	0	0	0·1472	0·1472	68
2	0	2	—	0·1721	—
1	1	4	—	0·1733	—
2	1	1	0·1901	0·1902	45
1	0	5	0·1926	0·1925	36
0	0	6	—	0·2242	—
2	1	3	0·2397	0·2401	64
2	0	4	0·2468	0·2469	38
2	2	0	0·2944	0·2944	20
1	1	6	0·2982	0·2978	36
2	2	2	—	0·3193	—
3	0	1	0·3399	0·3475	40
2	1	5		0·3397	
1	0	7		0·3420	
3	1	0	—	0·3680	—
2	0	6	—	0·3714	—

Table 7 (*cont.*)

h k l	$\sin^2 \theta_o$	$\sin^2 \theta_c$	I_o
3 0 3	—	0·3873	—
3 1 2	0·3928	0·3930	46
2 2 4		0·3941	
0 0 8	—	0·3986	—

Conclusion

The proposed structure formally resembles the crystal structure of the binary aluminides of alkaline earth metals as well as of the rare earth metals (*Strukturbericht*, 1937; Nowotny, 1942). The latter structure has been described alternatively with the unit cell in which 3*a* is taken for *a* and *c*/2 for *c*, in which case the space groups:

$$I\bar{4}2m\ (D_{2d}^{11}),\ I4mm\ (C_{4v}^{9}),\ I42\ (D_{4}^{9})\ \text{and}\ I4/mmm\,(D_{4h}^{17})$$

have been considered as possible. According to the criterion originally proposed by Frank & Kasper (1958) and modified by Cromer, Larson & Roof (1964), the silicon atoms in position 4(*e*) should be considered as neighbours of the central thorium atom. This leads to the interesting conclusion that the coordination number must be 18 (Fig. 1). The elongated coordination polyhedron is characterized by the two Th–Si distances which differ very much from the other sixteen. The biggest difference can be noticed in $ThMn_2Si_2$ and $ThCr_2Si_2$, while in the other cases it does not seem to be significant. This variable shape of the coordination polyhedron strongly suggests the existence of directional covalent bonds between the constituents and possibly the explicitly non-spherical shape of the largest atom in the structure, *viz.* thorium. In this case the metallic radius of thorium should be considered larger than the value 1·795 Å usually assumed (Pauling, 1956). It has been mentioned already (Krip'yakevich, 1963) that the formula of $BaAl_4$ should properly be written $BaAl_2^{I}Al_2^{II}$, because there are two distinct positions of the aluminum atoms. In our case such a distinction is realized, and this in turn enables us to seek for the existence of the ternary aluminides of the same structure type, with the same or some other transition metals. Another striking property of the structure is the variation of cell volume *versus* atomic number (Fig. 2). The contraction of the cell volume of the cobalt compound has apparently the same origin as in the case of the compound of $CoSi_2$ with $NiSi_2$, and may be therefore attributed to the change of bond type. The difference in both cases amounts approximately to 1%.

The existence of the copper compound in this series, together with the fact that attempts to prepare $ThZn_2Si_2$ failed, strongly supports the generally accepted concept of bond formation between the transition metals and electron-donating non-metals. Thus the formation of these compounds could be explained by the simultaneous filling of the inner electronic levels in thorium and transition metal atoms. Measurements which will be carried out of the electrical and magnetic properties of these compounds will bring additional data which may be useful in the interpretation of the nature of bonding.

Finally it should be mentioned that an analogous series of the isomorphous thorium germanides and some compounds of the ZrM_2Si_2 have been prepared in this laboratory. Crystallographic data of these compounds will be the subject of a separate paper.

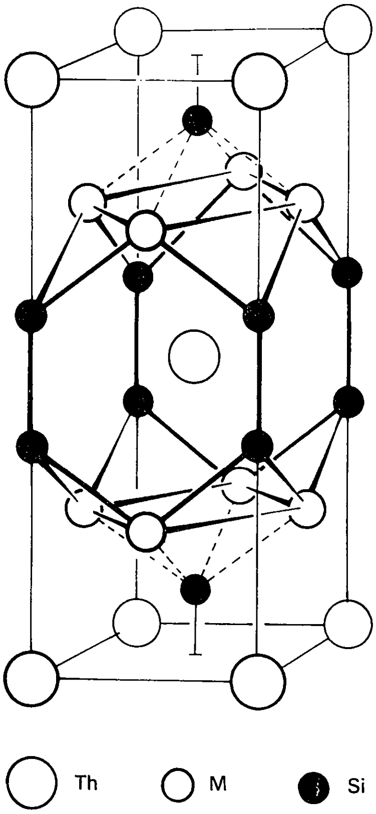

Fig. 1. Crystal structure of $ThMSi_2$.

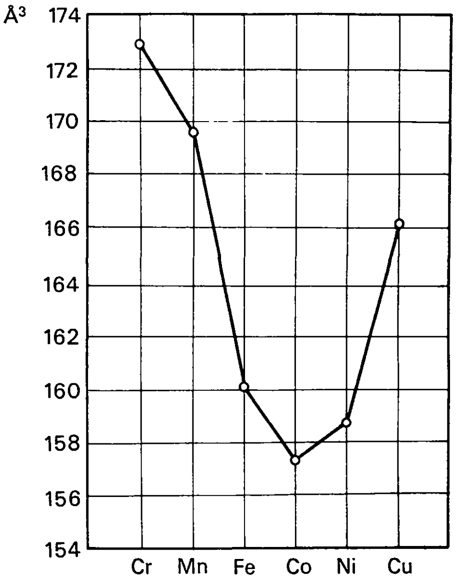

Fig. 2. Relation of unit-cell volume to atomic number.

Table 8. *Fractional coordinate, z,* α distances (Å) *from* Th *in position* 2(*a*) *and from* M *in position* 4(*d*) *to neighbouring atoms*

	M =	Cr	Mn	Fe	Co	Ni	Cu
	Z =	0·374	0·386	—	—	0·366	0·379
Th 2(*a*)	8 M 4(*d*)	3·328	3·304	3·179	3·160	3·139	3·208
	8 Si 4(*e*)	3·154	3·084	—	—	3·153	3·138
	2 Si 4(*e*)	3·956	4·050	—	—	3·496	3·738
M 4(*d*)	4 M 4(*d*)	2·859	2·843	2·855	2·839	2·882	2·902
	4 Si 4(*e*)	2·410	2·465	—	—	2·320	2·415

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The Crystal Structure of 2,7-Diacetoxy-*trans*-15,16-dimethyl-15,16-dihydropyrene

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The crystal is monoclinic $P2_1/a$. At room temperature $a=20{\cdot}07$, $b=7{\cdot}56$, $c=5{\cdot}88$ Å, $\beta=96{\cdot}52°$, $Z=2$, formula $C_{22}O_4H_{20}$.

The structure was determined from a three-dimensional Patterson synthesis, and refined by least-squares procedures. Two sets of intensity data were used independently. One was collected at room temperature with the use of a scintillation counter; the other was recorded on Weissenberg photographs at −130 °C, and estimated visually.

The 14 peripheral atoms of the pyrene nucleus are approximately coplanar, and appear to form an aromatic system.

Introduction

The molecule under examination ($C_{22}O_4H_{20}$, Fig. 1) is a novel aromatic system in which the methyl groups reside within the cavity of the 14-π-electron system (Boekelheide & Phillips, 1963). The crystal structure analysis was undertaken in order to provide information to aid in the investigation of the physical and chemical properties of such systems.

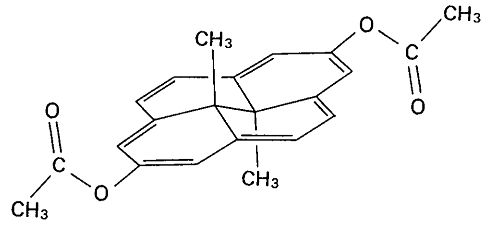

Fig. 1

Experimental

The elongated aspect of the molecule suggested that there would be significant anisotropy of thermal motion in the crystal and that it would be prudent to reduce this source of error by collecting intensity data at a reasonably low temperature. At the time of analysis, scintillation-counter techniques of data collection were available in this laboratory for use at room temperature only. Work at a lower temperature required the use of the less accurate photographic methods. The choice between the alternatives was so difficult that finally two sets of data were collected, one at −130 °C, using photographic methods, and one at room temperature, using the scintillation counter.