868. *The Preparation and Structure of Molybdenum Pentafluoride.*

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The preparation and purification of molybdenum pentafluoride are described. The structural unit of the solid has been determined, by *X*-ray single-crystal techniques, to be a tetramer with the molybdenum atoms at the corners of a square; the metal atoms are linearly linked by bridging fluorine atoms.

Of the four fluorides of molybdenum, only the hexafluoride is well known. Brief communications[1,2] have reported the preparation and some of the properties of the pentafluoride and tetrafluoride, and although more information is available about the trifluoride,[3-5] the evidence as to its purity and structure is conflicting.

Molybdenum pentafluoride was first isolated[1] from the reaction between elementary fluorine and molybdenum carbonyl at —65°, and until now this is the only direct reference to a preparative method although it can be inferred (cf. ref. 5) that others are known. The compound is conveniently prepared by reduction of the hexafluoride (*a*) by molybdenum or tungsten carbonyl at 25°, and (*b*) by molybdenum powder at 300—400°. A less pure product, contaminated with a large proportion of the oxytetrafluoride, is formed by the action of dilute fluorine on molybdenum powder at 400°.

Pure molybdenum pentafluoride is a yellow crystalline solid which melts at 67° to a viscous yellow liquid. As the temperature is raised the liquid becomes more mobile, but at about 150° the compound begins to disproportionate irreversibly to the hexafluoride and a solid phase which we believe to be the tetrafluoride. The dismutation is catalysed by borosilicate glass at lower temperatures, so that the liquid pentafluoride changes colour from yellow to green after a few hours in a glass apparatus. The extrapolated boiling point[2] is 211°, a value near that of other transition-metal pentafluorides. At 65° the compound has a vapour pressure of about 2 mm., while the oxytetrafluoride, $MoOF_4$, the chief impurity, has a vapour pressure of about 4 mm.

For the structure determination single crystals were set up in Pyrex glass capillaries as described below.

Experimental

Carbonyls were resublimed before use. Molybdenum hexafluoride was prepared from the elements.

Reduction of Molybdenum Hexafluoride with Molybdenum Carbonyl.—An excess of molybdenum hexafluoride was sublimed into a reaction bulb which contained a weighed quantity (0·5 g.) of the hexacarbonyl. The bulb was allowed to warm; just above the melting point of molybdenum hexafluoride the reaction began, and continued quietly with the evolution of carbon monoxide. When the carbonyl was consumed, the remaining hexafluoride was pumped off, and the apparatus was kept under a high vacuum while the temperature was gradually raised. At 60° molybdenum pentafluoride began to collect above the surface of the hot bath and at 100° distilled rapidly out of the vessel (Found: Mo, 49·9. Calc. for MoF_5: Mo, 50·3%). Green molybdenum tetrafluoride, amounting to about the same weight as the pentafluoride, remained in the bulb (Found: Mo, 56·6. Calc. for MoF_4: Mo, 55·8%).

Reduction of Molybdenum Hexafluoride with Tungsten Carbonyl.—The same technique was used as described above. Molybdenum pentafluoride was identified by its physical properties.

Reduction of Molybdenum Hexafluoride with Molybdenum.—Resublimed molybdenum hexafluoride was passed over molybdenum powder in a nickel tube at 300—400°. The pentafluoride was allowed to run from the tilted reaction vessel into a horizontal Pyrex receiver

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[1] Peacock, *Proc. Chem. Soc.*, 1957, 59.

[2] Cady and Hargreaves, *J.*, 1961, 1568.

[3] Gutmann and Emeléus, *J.*, 1949, 2979.

[4] Gutmann and Jack, *Acta Cryst.*, 1951, **4**, 244.

[5] Lavalle, Steele, Wilkinson, and Yackel, *J. Amer. Chem. Soc.*, 1960, **82**, 2433.

(A, Fig. 1); this technique allowed for the change in volume of the compound on solidification. The material was purified as described below (Found: Mo, 50·4. MoF_5 requires Mo, 50·3%).

Interaction of Fluorine and Molybdenum.—Elementary fluorine (6 l./hr.), diluted with oxygen-free nitrogen, was passed over molybdenum powder (50 g.) in a nickel vessel at 400°. White, yellow, and blue materials, solid and liquid, passed over into the first trap, which was cooled to $-60°$. On fractionation, the following materials were identified by their physical properties: molybdenum pentafluoride and molybdenum oxytetrafluoride (major components), and molybdenum hexafluoride (minor component).

Purification.—Molybdenum pentafluoride is easily separated from the more volatile hexafluorides by ordinary trap-to-trap distillation, and the problem is to separate it from the oxytetrafluoride, $MoOF_4$, b. p. 180°.

The impure sample of the pentafluoride, which had been stored under a vacuum, was held in the trap A (Fig. 1). The apparatus was dried by pumping out and baking under vacuum, and was maintained under black vacuum conditions during the experiment. The break-seal B was broken under vacuum with nickel balls held in C. The glass fragments and the nickel balls were returned to C which was then sealed from the rest of the vacuum line. As far as the point X the apparatus was now warmed to 65° with a heating tape, and eventually molybdenum pentafluoride began to appear as a yellow crystalline sublimate in D, which was held at room temperature by means of water-saturated cotton wool. Sublimation was continued from one section to another, until the more volatile oxyfluoride collected in the final section H, and sections E and F contained pure pentafluoride. The material in G, which still contained a little impurity, was retained for further purification with the next batch. Individual sections were sealed off at the constrictions, care being taken to see that these were absolutely clean inside and out before a flame was applied.

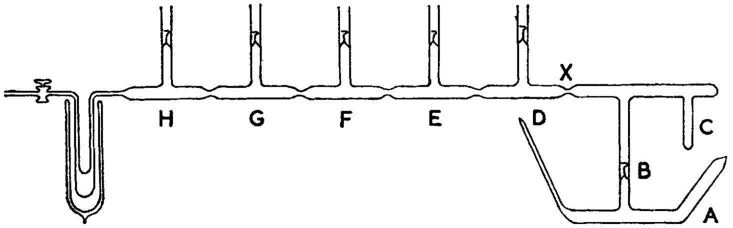

FIG. 1. Trap arrangement for the separation of molybdenum pentafluoride from the hexafluorides.

Filling of Capillaries.—Since molybdenum pentafluoride is hygroscopic it was necessary to seal crystals in Pyrex capillaries under vacuum; earlier attempts to coat crystals with polystyrene cement or to seal them in capillaries under dry air in a dry-box were not successful. The compound was sublimed into the bell-end of an *X*-ray capillary tube under black vacuum conditions, and the crystals were loosened from the glass surface by careful cooling with liquid air. By tapping the bell-end of the capillary or setting up vibrations with a file it was possible to transfer individual crystals into different sections of the capillary tube, which could then be sealed at suitable points over a micro-flame. The size of the crystals chosen was such that they lodged in the capillary so that they could be eventually set about crystallographic axes by the usual methods.

Density.—The density was measured by using a liquid-displacement method and a density bottle. The liquid chosen was perfluorofluorene which does not dissolve or react with molybdenum pentafluoride. The density bottle was filled and stoppered in a dry-box.

Crystal Data.—MoF_5, $M = 190·9$, monoclinic, $a = 9·61 \pm 0·01$, $b = 14·22 \pm 0·02$, $c = 5·16 \pm 0·01$ Å, $\beta = 94° 21' \pm 20'$, $V = 703$ Å^3, $D_m = 3·44$, $Z = 8$, $D_c = 3·61$, F(000) = 696. Space group, $C2/m$ (C_{2h}^3, No. 12). Cu-K_α radiation, single-crystal oscillation and Weissenberg photographs.

Reflections with $h + k \neq 2n$ were systematically absent, characteristic of space-groups $C2$, Cm, and $C2/m$. The space-group was assumed to be $C2/m$, and this was confirmed by the subsequent success of the analysis. The linear absorption coefficient is 328 cm.$^{-1}$. The crystals studied had dimensions of about 0·03 mm. and since the crystals were small absorption errors were ignored.

Structure Determination.—Single crystals were used to obtain intensity data for the $hk0$ and $0kl$ zones. The intensities of the spots were difficult to estimate; for the $hk0$ zone the spots were small, and for the $0kl$ zone they were elongated. The usual multiple-film technique was applied, and relative intensities were estimated by visual comparison with a standard scale. Values of F^2 were obtained by correction for Lorentz and polarisation factors. 63 of the 90 possible $hk0$ reflections and 33 out of the 55 $0kl$ reflections were observed.

The $hk0$ projection was solved first as it promised the best resolution of the atoms. A Patterson synthesis was calculated and was interpreted to give the positions of the molybdenum atoms. The phases determined from the molybdenum co-ordinates were used for the first Fourier synthesis, and the resultant electron-density map showed the positions of all the fluorine atoms. Structure factors were calculated by using the scattering factors of Berghuis *et al.*[6] for fluorine, and of James and Brindley [7] for molybdenum, values being taken for un-ionised atoms (cf. ref. 4). At this stage the discrepancy factor R was 25% (for observed reflections only). Refinement by Fourier synthesis in two cycles reduced the R value to 15·6% and fixed the signs of all but five structure factors. A single isotropic temperature factor $B = 2{\cdot}5$ Å^2 was used.

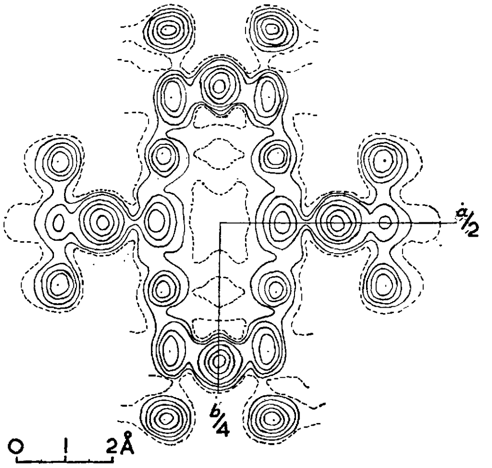

FIG. 2. Electron-density projection along [001]. Contours at 1e/Å^2, except in molybdenum atoms at 10e/Å^2.

The least-squares procedure involving co-ordinates and different isotropic temperature factors for molybdenum and fluorine was next applied to the observations. The observed structure factors were all given the same weight, and those not observed were omitted. Refinement was terminated when shifts in co-ordinates became negligible. This led to isotropic temperature factors $B_{\text{Mo}} = 2{\cdot}2$ Å^2, $B_{\text{F}} = 4{\cdot}2$ Å^2, and $R = 12{\cdot}4\%$. The final electron-density projection along [001] is shown in Fig. 2.

The $0kl$ projection was solved by the methods outlined above, and for these reflections a final R value of 12·0% was obtained (for observed reflections only). In the least-squares procedure, the isotropic temperature factors were found to agree with those for the $hk0$ zone ($\pm 0{\cdot}1$ Å^2). If the unobserved reflections were given a structure amplitude of half the minimum observable value for the particular angle of reflection, the R values were 15·6% for the $hk0$ and 16·4% for the $0kl$ zone.

Weissenberg photographs of the $h0l$ zone were also obtained but the spots were unsuitable for accurate intensity estimations. A comparison of the intensities of some $h0l$ and corresponding $\bar{h}0l$ reflections was possible however, and allowed atomic positions to be fixed with respect to the conventional a and c directions.

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[6] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

[7] James and Brindley, *Z. Krist.*, 1931, **78**, 470.

TABLE 1.

Atomic parameters.

Atom	x/a	y/b	z/c	σ (Å)
Mo(1)	0	0·204	1·000	0·001
Mo(2)	0·262	0	0·745	0·001
F(1)	0·135	0	0·500	0·050
F(2)	0·353	0	0·970	0·050
F(3)	0·360	0·091	0·627	0·018
F(4)	0·128	0·103	0·871	0·015
F(5)	−0·109	0·188	0·700	0·045
F(6)	0·128	0·290	0·871	0·015

TABLE 2.

Observed and calculated structure factors.

$h\ k\ l$	$\lvert F_0\rvert$	F_c
0 0 1	166	169
2	<	$\overline{5}$
3	93	99
4	87	106
5	<25	17
6	<20	7
0 2 0	45	32
1	177	$\overline{155}$
2	130	$\overline{148}$
3	69	$\overline{63}$
4	<25	23
5	37	$\overline{43}$
6	41	$\overline{64}$
0 4 0	194	194
1	66	60
2	26	$\overline{27}$
3	27	36
4	90	114
5	<26	19
6	<18	17
0 6 0	140	131
1	<17	11
2	71	$\overline{64}$
3	34	28
4	91	101
5	<24	5
6	<15	$\overline{24}$
0 8 0	29	28
1	69	$\overline{53}$
2	103	$\overline{95}$
3	52	$\overline{51}$
4	<26	23
5	<22	$\overline{23}$
0 10,0	236	239
1	91	78
2	<26	6
3	59	56
4	65	77
5	<18	17
0 12,0	<23	15
1	80	$\overline{71}$
2	106	$\overline{96}$
3	36	$\overline{31}$
4	<21	7
0 14,0	99	81
1	37	28
2	<25	$\overline{7}$
3	<21	$\overline{23}$
4	34	60
0 16,0	<22	32
1	<21	$\overline{7}$
2	35	$\overline{38}$
3	<13	4
0 18,0	<13	16
1	<11	12
1 1 0	51	46
3	136	$\overline{143}$
5	116	116
7	87	$\overline{78}$
9	<19	27
11	<21	11
13	52	$\overline{49}$
15	37	40
17	29	$\overline{31}$
2 0 0	9	$\overline{14}$
2	236	$\overline{281}$
4	99	$\overline{77}$
6	109	$\overline{81}$
8	183	$\overline{161}$
10	<21	$\overline{6}$
12	136	$\overline{117}$
14	<23	$\overline{19}$
16	<19	$\overline{39}$
18	33	$\overline{47}$
3 1 0	61	78
3	68	$\overline{62}$
5	130	140
7	98	$\overline{88}$
9	80	65
11	<23	12
13	<23	$\overline{7}$
15	54	52
17	28	$\overline{30}$
4 0 0	32	28
2	<14	11
4	139	141
6	129	105
8	35	24
10	78	67
12	<23	$\overline{7}$
14	56	68
16	36	32
5 1 0	33	28
3	96	$\overline{94}$
5	66	50
7	132	$\overline{105}$
9	38	12
11	40	$\overline{31}$
13	43	$\overline{34}$
15	30	22
6 0 0	<19	26
2	106	$\overline{120}$
4	45	36
6	68	$\overline{59}$
8	88	$\overline{83}$
10	<23	12
12	83	$\overline{75}$
14	<16	$\overline{6}$
7 1 0	56	50
3	<21	$\overline{13}$
5	105	89
7	<23	$\overline{8}$
9	52	48
11	<21	22
13	<16	$\overline{9}$
15	35	43
8 0 0	161	167
2	<23	$\overline{3}$
4	80	70
6	46	49
8	<23	6
10	90	94
12	<16	$\overline{4}$
14	27	44
9 1 0	<23	$\overline{7}$
3	73	$\overline{72}$
5	<23	18
7	60	$\overline{65}$
9	<19	$\overline{5}$
11	<14	$\overline{11}$
10,0 0	<21	$\overline{5}$
2	106	$\overline{84}$
4	<21	$\overline{15}$
6	<19	$\overline{25}$
8	69	$\overline{56}$
10	<12	5
11,1 0	40	41
3	<16	$\overline{5}$
5	59	63
7	<12	$\overline{10}$
12, 0 0	<46	42
2	<14	$\overline{5}$
4	27	32

TABLE 3.

Interatomic distances in molybdenum pentafluoride.

(1) *Intramolecular*

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Mo(1)–Mo(1′)	5·80 ± 0·006	Mo(2)–F(2)	1·66 ± 0·10	F(4)–F(4″)	2·93 ± 0·08
Mo(2)–Mo(2′)	5·86 ± 0·006	Mo(2)–F(3)	1·74 ± 0·04	F(3)–F(3′)	2·59 ± 0·08
Mo(1)–F(4)	2·04 ± 0·04	F(6)–F(6′)	2·89 ± 0·08	F(3)–F(4)	2·65 ± 0·08
Mo(2)–F(4)	2·09 ± 0·04	F(6)–F(4)	2·66 ± 0·08	F(3)–F(1)	2·56 ± 0·14
Mo(1)–F(5)	1·82 ± 0·09	F(6)–F(5)	2·89 ± 0·14	F(3)–F(2)	2·45 ± 0·14
Mo(1)–F(6)	1·89 ± 0·04	F(4)–F(5)	2·78 ± 0·14	F(2)–F(4)	2·63 ± 0·14
Mo(2)–F(1)	1·69 ± 0·10	F(4)–F(4′)	2·89 ± 0·08	F(1)–F(4)	2·42 ± 0·14

(2) *Intermolecular*

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
F(3)–F(3)	3·01 ± 0·08	F(5)–F(5)	3·79 ± 0·18	F(3)–F(5)	3·18 ± 0·14
F(2)–F(2)	3·12 ± 0·20	F(5)–F(6)	2·59 ± 0·14	F(4)–F(6)	3·02 ± 0·08
F(1)–F(1)	2·59 ± 0·20	F(2)–F(6)	3·00 ± 0·14		

(3) *Bond angles*

F(4)–Mo(1)–F(4′)	90·0° ± 1°	F(4)–Mo(2)–F(4′)	90·1° ± 1°	F(1)–Mo(2)–F(3)	96·5° ± 2·5°
F(6)–Mo(1)–F(6′)	99·7 ± 1·5	F(3)–Mo(2)–F(3′)	96·2 ± 1·5	F(2)–Mo(2)–F(3)	92·2 ± 2·5
F(5)–Mo(1)–F(4)	88·0 ± 2	F(1)–Mo(2)–F(4)	80·0 ± 2·5	F(1)–Mo(2)–F(2)	164·7 ± 3
F(5)–Mo(1)–F(6)	102·3 ± 2	F(2)–Mo(2)–F(4)	88·6 ± 2·5	Mo(1)–F(4)–Mo(2)	180·0 ± 2
F(5)–Mo(1)–F(5′)	165·8 ± 2·5				

In the space-group *C*2/*m* the molybdenum atoms occupy the four-fold positions (*i*) and (*g*) [8] and the fluorine atoms two sets of four-fold positions (*i*) and four sets of eight-fold positions (*j*). The estimated standard deviations of the atomic co-ordinates were calculated by Cruikshank's method.[9] The final atomic parameters with their estimated standard deviations (σ) are given in Table 1 and the observed and calculated structure factors in Table 2.

Description of the Structure.—In the square tetrameric unit of the molybdenum pentafluoride structure (Fig. 3 and Table 3) there are three different orders of Mo–F bond length: (*a*) about 1·85 Å, the distance from Mo(1) to the neighbouring singly-bound fluorine atoms, (*b*) about 1·70 Å, the distance from Mo(2) to the remaining singly-bound fluorine atoms, and (*c*) about 2·06 Å, the distance from the molybdenum atoms to the bridging fluorine atoms. The average of (*a*) and (*b*), 1·78 Å, is not far from the Mo–F separation in NaMoF$_6$, *viz.* 1·74 ± 0·03 Å,[10] and is shorter than either the sum of the single-bond covalent radii (2·08 Å) or the sum of the ionic radii (2·03 Å) of the atoms.[11] The long-bond distance (*c*) is close to the sum of the covalent radii. The bond angles measured about Mo(1) and Mo(2) are similar, a point which suggests that the observed difference between (*a*) and (*b*) is probably not significant.

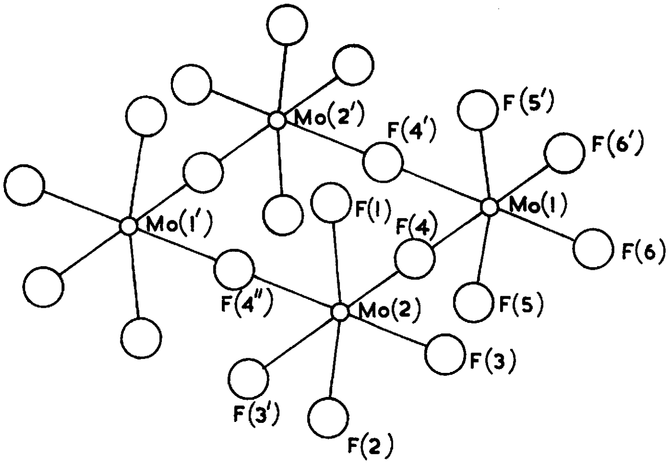

FIG. 3. The square tetrameric unit of the molybdenum pentafluoride structure.

DISCUSSION

There is little structural information on solid metal pentahalides in general, and most refers to halides other than fluorides. However, the structure of molybdenum pentafluoride can be usefully compared to that of the pentachloride,[12] in which dimeric units contain two bridging chlorine atoms with an Mo–Cl–Mo bond angle of 98·6°, a Cl–Cl distance (between bridging chlorine atoms) of 3·29 Å, and a Mo–Mo distance of 3·84 Å. Each molybdenum atom lies in an equivalent environment of chlorine atoms. Although the structure as a whole is very different from that of molybdenum pentafluoride, there are points of similarity. First, the shape of the molybdenum hexachloride octahedra is nearly the same as that of the MoF$_6$ octahedra in MoF$_5$. Secondly, the bridging Mo–Cl bond distance (2·53 Å) is 0·29 Å longer than the normal Mo–Cl bond length (2·24 Å); the

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[8] "International Tables for *X*-ray Crystallography," Kynoch Press, Birmingham, Vol. 1, 1952, p. 95.

[9] Cruikshank, *Acta Cryst.*, 1949, **2**, 65.

[10] Edwards and Peacock, *J.*, 1961, 4253.

[11] Distances estimated from figures given in Pauling, "The Nature of the Chemical Bond," 3rd edn., Oxford University Press, London, 1960, pp. 252 *et seq.* and 511 *et seq.*

[12] Sands and Zalkin, *Acta Cryst.*, 1959, **12**, 723.

corresponding average difference in molybdenum pentafluoride is 0·28 Å. The sum of the ionic radii of Mo^{5+} and Cl^- is 2·49 Å, and that of the covalent radii is 2·34 Å, so that the observed normal molybdenum–halogen bond length is short, like those in MoF_5 and $NaMoF_6$.

Other MX_5 structures include the ionic phosphorus pentachloride and pentabromide types, which have not so far been found among transition-metal halides, and the two forms of uranium pentafluoride. Uranium pentafluoride, which has physical properties very different from molybdenum pentafluoride, exists in two crystalline modifications, one of which (α-UF_5) contains six co-ordinated uranium atoms and infinite chains of UF_6 octahedra linked by bridging fluorines which are said to be linearly bonded just as in molybdenum pentafluoride.[13] Unfortunately, this particular structure has not been determined with sufficient accuracy to allow certainty of the fluorine positions.

The transition-metal pentafluorides of the second and third periods constitute a homogeneous group of compounds with similar melting and boiling points, and these properties point to structural similarities. Besides molybdenum pentafluoride, we have examined, with a view to subsequent analysis, *X*-ray powder patterns of a number of pentafluorides. From these it is evident that niobium and tantalum pentafluorides are isostructural with molybdenum pentafluoride, that ruthenium and osmium pentafluoride are isostructural with one another, but that rhenium pentafluoride (in the absence of technetium pentafluoride), the least stable member, stands alone. A preliminary single-crystal study in these laboratories has confirmed the similarity of niobium pentafluoride to molybdenum pentafluoride, and has indicated that ruthenium pentafluoride possesses a distorted version of the molybdenum pentafluoride structure. Since this type of structure could also be adopted by oxyfluorides such as molybdenum and rhenium oxytetrafluorides, it will be necessary to bring these also within the scope of the investigation.

Liquid antimony pentafluoride has been shown from nuclear magnetic resonance data[14] to have bridging Sb–F–Sb bonds arranged *cis* to one another just as in the molybdenum pentafluoride structure. Such bonds are probably also present in liquid transition-metal pentafluorides, since, like antimony pentafluoride, they are viscous. Other properties which may depend on bridging fluorine bonds are magnetism and colour (cf. refs. 15 and 16).

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[13] Zachariasen, *Acta Cryst.*, 1949, **2**, 65.
[14] Hoffman, Holder, and Jolly, *J. Phys. Chem.*, 1958, **62**, 364.
[15] Hargreaves and Peacock, *J.*, 1960, 1099.
[16] Hargreaves and Peacock, *J.*, 1960, 2618.