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Comparison of the frequencies of crystallographic space groups in organo-lanthanide and -actinide compounds

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Abstract

Bibliographic and numeric data on 1540 organo-lanthanide and 895 organo-actinide crystalline compounds were derived from the *Cambridge Structural Database*. After removal of the double entries, the compounds were classified into the 230 crystallographic space groups according to their space-group numbers, and the relative frequency of occurrence of each space group was then determined.

10.0% of the lanthanide and 8.4% of the actinide compounds fall in space groups of tetragonal or higher symmetry. In both cases, only 71 of the space groups have at least one entry. Approximately two-thirds of the compounds crystallize in three space groups: 34.1% of the lanthanides in $P2_1/c$ (actinides: 38.5%), 22.1% (20.5%) in $P\bar{1}$ and 8.3% (9.0%) in $C2/c$; in contrast, there are 46 space groups in the lanthanide group with five or fewer compounds assigned to them (55 for the actinides).

The distribution of the lanthanides into the different crystal families corresponds well to that of the actinides. If the data are compared with a study on the space-group frequencies for organic compounds (Mighell et al., *Acta Crystallogr., A39* (1983), 737–740) there are a number of important differences: lanthanides and actinides tend to crystallize more in the triclinic crystal family than the organic compounds (22.6% for lanthanides and 21.0% for actinides vs. 14.8% for organic compounds) and less in the orthorhombic crystal family (15.4% for lanthanides and 17.0% for actinides vs. 25.8% for organic compounds). There is an increase in the number of compounds crystallizing in one of the centrosymmetric space groups (78.5% for lanthanides and 81.7% for actinides vs. 70.4% for organic compounds) and a decrease for the enantiomorphic space groups (11.5% for lanthanides and 10.1% for actinides vs. 23.1% for organic compounds). The number of compounds crystallizing in one of the symmorphic space groups is higher (27.9% for lanthanides and 24.7% for actinides vs. 18.6% for organic compounds), which corroborates the fact that the number of compounds crystallizing in the triclinic system has increased.

Keywords: Crystallographic space groups; Organo-actinides; Organo-lanthanides

1. Introduction

Mighell et al. [1] reported the space-group frequencies for organic compounds (i.e. carbon-containing compounds) up to 1981. Donohue [2] revised the distribution for those space groups that do not contain any symmetry operations of the second kind (i.e. inversion centers or mirror planes). Space groups which are rare for organic structures have been analysed in a series of papers by Wilson [3–5]. Recently the space-group frequencies of proteins and of organic compounds with more than one formula unit in the asymmetric unit have been reported by Padmaja et al. [6].

The present study reports on the comparison of the space-group frequencies of crystal structures of organo-lanthanide and organo-actinide compounds. The data are also compared with the distribution for all organic compounds.

2. Methodology

The bibliographic and numeric data were retrieved from the October 1993 release of the *Cambridge Structural Database* (CSD Version 5.06, which contains 114924 entries) [7]. This database contains information on organic and organometallic compounds and metal complexes whose structures have been established by single-crystal X-ray or neutron diffraction. The query was defined in such a way that all entries containing a lanthanide or actinide atom were obtained. No search restrictions were ensured, so that compounds occurring twice or more in the database were retrieved (vide infra). For the purpose of this work, the item names for the number of atomic coordinates (COOR), for the occurrence of disorder (DISO) or errors (ERRO), for possible qualifying phrases of interest (QUAL) or general remarks (REMA), for the Herman–Mauguin space-

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group symbol (SPAC) and number (SPGN), for the temperature (TEMP) at which the crystal measurement was performed and the number of molecules in the unit cell (ZVAL) were explicitly printed out, in addition to the reference code (REFC) of the compound name (COMP) and its formula (FORM), the author(s) (AUTH) and the information where the publication can be found (flags CODE, VOLU, PAGE and YEAR).

Each entry in the CSD is assigned a unique eight-character reference code (usually abbreviated to 'refcode'). The first six (alphabetic) characters define the compound; the final two (numeric) characters describe the publication history. Different entries concerning the same chemical structure have refcodes which differ only in the last two characters. The numeric characters seven and eight distinguish multiple studies of the same structure: character seven ties together all entries with at least one common author; character eight identifies the entry uniquely.

For example DEURNE is the refcode given to the first entry for this structure described by author(s) "A". DEURNE10 is then the refcode given to an update report from author(s) "A". The refcode DEURNE01 denotes the first entry for this structure described by author(s) "B". A possible update report from author(s) "B" will receive refcode DEURNE11.

In the cases in which there was little doubt that authors "A" and "B" submitted their publication at approximately the same time but to different journals, so that the crystal structure occurs twice in the CSD (e.g. as DEURNE and DEURNE01), only one entry has been retained.

In many of the cases of refcodes having more than one entry, ZYXWVU will be a preliminary communication and ZYXWVU10 will be a full report superseding ZYXWVU. In order to avoid biased results, the first entry has not been taken into account. On the other hand, ZYXWVU01 may indicate another modification, a measurement at reduced temperature or a new refinement in another space group. In the former two cases, both entries have been taken into account, since examples of compounds which crystallize in two different crystal families or compounds which undergo a temperature-dependent phase transition are known. In the latter case only the most recent refinement has been implemented in the statistics.

Although there are only 230 possible space groups, space-group symbols other than those published in Vol. A of the *International Tables for Crystallography* [8] are frequently found in literature dealing with crystal-structure determination. This is a direct consequence of the possibility of having various settings and choices of the unit cell in a crystal. Changes of the basis vectors (or axis transformations) involve not only permutations of axes, conserving the shape of the cell, but also transformations which lead to different cell shapes and even to multiple cells. Examples of transformations of the first type are found in the monoclinic and the orthorhombic system. In the former system, two permutations of the basis vectors are possible for each choice of the unique axis (for instance, permutating the *a* and the *c* axis when the *b* axis has been considered as the unique axis) and, in the latter system, six permutations of the basis vectors are possible. Examples of transformations of the second type are found in the triclinic, the tetragonal and the hexagonal families. In the triclinic system a primitive unit cell (*P*) can always be selected; in some cases, however, it may be advantageous to select a larger cell, with *A*, *B*, *C*, *I* or *F* centering. The hexagonal crystal family contains the trigonal as well as the hexagonal crystal system. Both systems are described in a hexagonal lattice, but in the trigonal system there are seven space groups which can also be described onto rhombohedral axes.

Changes of the basis vectors generally cause changes of the Hermann–Mauguin space-group symbol (it may be noted that the Schoenflies symbol remains invariant). However, since the Hermann–Mauguin symbol for the standard setting of a space group and the extended Hermann–Mauguin symbols for the non-standard settings of this space group all have the same space-group number, the frequencies will be discussed with respect to the space-group numbers rather than to the symbols.

3. Results

In total the data on 1540 organo-lanthanide and 895 organo-actinide crystal structures were retrieved from the CSD. In six lanthanide and four actinide cases the space group is not known. Removal of double entries (vide supra) leads to 1429 lanthanide and 813 actinide compounds.

In the light of this work, it should be noted that two entries have been omitted in the organo-lanthanide data set because the authors were performing the refinement in non-centrosymmetric space groups; in this case the redetermined crystal structures have been retained [9–10]. The data file also mentions the re-refinement of a third compound by Marsh [9]. In the organo-actinide data set, two entries have been removed: in one case Schomaker and Marsh [11] redetermined the structure after changing the Laue symmetry; in the other case Marsh and Herbstein [10] added a center of symmetry.

For both data sets thus obtained, the number of compounds crystallizing in a space group with a given number were determined, and the results before (column marked "A") and after (column marked "C") removal of the double entries are given in Table 1. Since the number of entries is different for the two

Table 1
Space-group frequencies for organo-lanthanide and organo-actinide crystalline compounds

SPGN	U	S	E	C	Lanthanides						Actinides						Org %
					A	%	*C*	%	*D*	%	*A*	%	*C*	%	*D*	%	
Triclinic					**345**	**22.4**	**323**	**22.6**	**330**	**20.8**	**184**	**20.6**	**171**	**21.0**	**175**	**19.6**	**14.8**
1		*	*		7	0.5	7	0.5	14	0.9	4	0.4	4	0.5	8	0.9	1.0
2		*		*	338	21.9	316	22.1	316	19.8	180	20.1	167	20.5	167	18.7	13.7
Monoclinic					**799**	**51.9**	**743**	**52.0**	**811**	**51.0**	**482**	**53.9**	**436**	**53.6**	**457**	**51.1**	**53.7**
3		*	*		2	0.1	1	0.1	2	0.1							
4			*		60	3.9	55	3.8	110	6.9	20	2.2	19	2.3	38	4.2	6.7
5		*	*		12	0.8	12	0.8	24	1.5	2	0.2	2	0.2	4	0.4	0.9
7					4	0.3	4	0.3	4	0.3	5	0.6	5	0.6	5	0.6	0.4
8		*			2	0.1	2	0.1	2	0.1	2	0.2	2	0.2	2	0.2	0.1
9					26	1.7	24	1.7	24	1.5	10	1.1	8	1.0	8	0.9	1.0
11				*	14	0.9	13	0.9	13	0.8	7	0.8	6	0.7	6	0.7	0.8
12		*		*	12	0.8	11	0.8	11	0.7	3	0.3	3	0.4	3	0.3	0.7
13				*	17	1.1	16	1.1	16	1.0	5	0.6	5	0.6	5	0.6	0.5
14	*			*	525	34.1	487	34.1	487	30.6	342	38.2	312	38.5	312	34.9	36.0
15				*	125	8.1	118	8.3	118	7.4	86	9.6	74	9.0	74	8.3	6.6
Orthorhombic					**237**	**15.4**	**220**	**15.4**	**274**	**17.2**	**148**	**16.5**	**138**	**17.0**	**173**	**19.3**	**25.8**
18	*		*								2	0.2	2	0.2	4	0.4	0.6
19	*		*		57	3.7	53	3.7	106	6.6	32	3.6	32	3.9	64	7.2	11.6
20	*		*		1	0.1	1	0.1	2	0.1							0.3
24			*								1	0.1	1	0.1	2	0.2	
26					1	0.1	1	0.1	1	0.1							
27					1	0.1	1	0.1	1	0.1							
29					10	0.6	9	0.6	9	0.6	6	0.7	6	0.7	6	0.7	0.8
31					2	0.1	2	0.1	2	0.1	2	0.2	2	0.2	2	0.2	
32											1	0.1	1	0.1	1	0.1	
33					37	2.4	33	2.3	33	2.1	15	1.7	12	1.5	12	1.3	1.8
36					5	0.3	4	0.3	4	0.3	4	0.4	3	0.4	3	0.3	
38		*			1	0.1	1	0.1	1	0.1							
40											1	0.1	1	0.1	1	0.1	
41											1	0.1	1	0.1	1	0.1	
42		*									2	0.2	2	0.2	2	0.2	
43	*				14	0.9	13	0.9	13	0.8	6	0.7	6	0.7	6	0.7	0.8
44		*									1	0.1	1	0.1	1	0.1	
52	*		*		4	0.3	4	0.3	4	0.3	1	0.1	1	0.1	1	0.1	
53				*							2	0.2	2	0.2	2	0.2	
56	*			*	8	0.5	8	0.6	8	0.5	4	0.4	4	0.5	4	0.4	0.3
57				*	1	0.1	1	0.1	1	0.1	1	0.1	1	0.1	1	0.1	0.2
58				*	2	0.1	2	0.1	2	0.1	1	0.1	1	0.1	1	0.1	0.1
60	*			*	32	2.1	29	2.0	29	1.8	10	1.1	10	1.2	10	1.1	1.2
61	*			*	37	2.4	35	2.4	35	2.2	28	3.1	23	2.8	23	2.6	4.3
62				*	19	1.2	18	1.3	18	1.1	19	2.1	19	2.3	19	2.1	1.9
63				*	1	0.1	1	0.1	1	0.1	1	0.1	1	0.1	1	0.1	0.2
64				*	4	0.3	4	0.3	4	0.3	2	0.2	2	0.2	2	0.2	0.3
65		*		*							1	0.1	1	0.1	1	0.1	
70	*			*							4	0.4	3	0.4	3	0.3	
Tetragonal					**46**	**3.0**	**45**	**3.1**	**57**	**3.6**	**45**	**5.0**	**40**	**4.9**	**52**	**5.8**	**2.9**
76	*		*								1	0.1	1	0.1	1	0.1	
78	*		*												*1*	*0.1*	
81		*									1	0.1	1	0.1	1	0.1	
82		*			5	0.3	4	0.3	4	0.3	4	0.4	4	0.5	4	0.4	0.2
85	*			*	2	0.1	2	0.1	2	0.1	4	0.4	4	0.5	4	0.4	0.1
86	*			*	2	0.1	2	0.1	2	0.1	2	0.2	2	0.2	2	0.2	0.2
87		*		*	3	0.2	3	0.2	3	0.2							0.1
88	*			*							5	0.6	5	0.6	5	0.6	0.3
92	*		*		8	0.5	8	0.6	10	0.6	6	0.7	5	0.6	9	1.0	0.3
93	*		*		1	0.1	1	0.1	2	0.1							
94	*		*								2	0.2	1	0.1	2	0.2	
96	*		*		2	0.1	2	0.1	10	0.6	6	0.7	4	0.5	9	1.0	0.2
97		*	*		1	0.1	1	0.1	2	0.1							

(*continued*)

Table 1 (*continued*)

SPGN	U	S	E	C	Lanthanides						Actinides						Org %
					A	%	*C*	%	*D*	%	*A*	%	*C*	%	*D*	%	
98	*		*								1	0.1	1	0.1	2	0.2	
104					12	0.8	12	0.8	12	0.8							
113					2	0.1	2	0.1	2	0.1							
114	*				1	0.1	1	0.1	1	0.1	3	0.3	3	0.4	3	0.3	0.2
116					1	0.1	1	0.1	1	0.1							
118											1	0.1	1	0.1	1	0.1	
119		*			1	0.1	1	0.1	1	0.1							
121		*			1	0.1	1	0.1	1	0.1	1	0.1	1	0.1	1	0.1	
122					2	0.1	2	0.1	2	0.1	2	0.2	2	0.2	2	0.2	
126	*			*							1	0.1	1	0.1	1	0.1	
130	*			*	1	0.1	1	0.1	1	0.1							
136				*							3	0.3	2	0.2	2	0.2	
137	*			*							1	0.1	1	0.1	1	0.1	
139		*		*	1	0.1	1	0.1	1	0.1	1	0.1	1	0.1	1	0.1	
Trigonal					**52**	**3.4**	**51**	**3.6**	**69**	**4.3**	**19**	**2.1**	**18**	**2.2**	**22**	**2.5**	**1.6**
144			*		1	0.1	1	0.1	2	0.1							
145			*		1	0.1	1	0.1	2	0.1							
146		*	*		6	0.4	6	0.4	12	0.8	3	0.3	3	0.4	6	0.7	0.1
147		*		*							2	0.2	1	0.1	1	0.1	
148		*		*	8	0.5	7	0.5	7	0.4	5	0.6	5	0.6	5	0.6	0.4
152	*		*		2	0.1	2	0.1	2	0.1	1	0.1	1	0.1	1	0.1	0.1
154	*		*						*2*	*0.1*					*1*	*0.1*	
155		*	*		8	0.5	8	0.6	16	1.0							
159					2	0.1	2	0.1	2	0.1	2	0.2	2	0.2	2	0.2	
160		*			5	0.3	5	0.3	5	0.3	2	0.2	2	0.2	2	0.2	
161					13	0.8	13	0.9	13	0.8	2	0.2	2	0.2	2	0.2	0.1
163				*	2	0.1	2	0.1	2	0.1	1	0.1	1	0.1	1	0.1	
166		*		*	1	0.1	1	0.1	1	0.1							
167				*	3	0.2	3	0.2	3	0.2	1	0.1	1	0.1	1	0.1	0.1
Hexagonal					**46**	**3.0**	**39**	**2.7**	**40**	**0.5**	**6**	**0.7**	**5**	**0.6**	**7**	**0.8**	**0.7**
169	*		*								1	0.1	1	0.1	1	0.1	
170	*		*												*1*	*0.1*	
173	*		*		4	0.3	4	0.3	4	0.3							0.1
176				*	39	2.5	32	2.2	32	2.0	1	0.1	1	0.1	1	0.1	0.3
178	*		*		1	0.1	1	0.1	1	0.1					1	0.1	
179	*		*						1	0.1	1	0.1	1	0.1	1	0.1	
186					1	0.1	1	0.1	1	0.1	2	0.2	1	0.1	1	0.1	
190					1	0.1	1	0.1	1	0.1	1	0.1	1	0.1	1	0.1	
Cubic					**9**	**0.6**	**8**	**0.6**	**9**	**0.6**	**7**	**0.8**	**5**	**0.6**	**9**	**1.0**	**0.5**
196		*	*		2	0.1	1	0.1	2	0.1							
198	*		*								6	0.6	4	0.5	8	0.9	
200		*		*	3	0.2	3	0.2	3	0.2							
205	*			*	2	0.1	2	0.1	2	0.1							0.1
217		*			1	0.1	1	0.1	1	0.1							
220	*				1	0.1	1	0.1	1	0.1							
221		*		*							1	0.1	1	0.1	1	0.1	
Unknown					**6**	**0.4**	**0**	**0**	**0**	**0**	**4**	**0.4**	**0**	**0**	**0**	**0**	**0**

data sets, the relative abundancies have also been tabulated. In order to make a comparison with all organic compounds, the relative abundancies have been calculated from the paper of Mighell et al. [1]; in the cases in which the frequency is less than 0.05%, no value is given (this corresponds to 14 or less entries).

Only space groups having at least one entry either in the data set of the organo-lanthanides or in the data set of the organo-actinides have been included in Table 1.

The data on the different crystal families are summarized in bold type at the start of each crystal family.

In the second column an asterisk indicates whether a space group is unambiguously determined from the symmetry of the diffraction pattern and from the systematic absences (column U), and in the following columns an asterisk denotes the type of space group: S for the symmorphic (the symmetry operations do not contain translations), E for the enantiomorphic (no inversion centers or mirror planes present) and C for the centrosymmetric (inversion center present) space groups.

4. Discussion

It should be noted that this type of data must be taken with some caution since only 69 of the 230 crystallographic space groups are uniquely determined from the symmetry of the diffraction pattern and from systematic absences. In some cases it can occur that a compound crystallizes in such a way that there are two or more crystallographically independent molecules in the asymmetric part of the unit cell (vide infra). However, care should be taken with this kind of data, as it may well be that a higher-symmetry space group has been overlooked. Detailed analyses of several cases in which crystal structures have been reported in space groups of unnecessarily low symmetry have been carried out; recent examples can be found in the following references: Marsh and Herbstein [12], Marsh [13–15], Baur and Tillmanns [16] and De Ridder [17]. As a consequence, one has to allow for the fact that certain space-group frequencies may be under- or overestimated. These errors are due to compounds described in (a) correct crystal system but incorrect space group, (b) incorrect crystal system and incorrect space group [1]. An unequivocal space-group determination of a given crystal can only be through the least-squares refinement of the structure in various candidate space groups and distinguishing between them through significance tests [18].

4.1. General aspects

Inspection of the data of Table 1 reveals that not all of the space groups are occupied: for both data sets, only 71 of the 230 space groups have at least one entry. It can also be observed that space groups which are occupied in the organo-lanthanide data set are unoccupied in the organo-actinide data set and vice versa, and this especially for those space groups having five or fewer compounds assigned to them. Of the latter there are 46 space groups in the lanthanide group and 55 for the actinides.

In the study of Mighell et al. [1] it was not indicated whether the data were corrected for double entries. If the relative frequencies of all entries are compared with the corrected values for each crystal family within both data sets, the largest difference (0.5%) is observed for the orthorhombic family of the organo-actinides. The largest difference for a space group is observed for $C2/c$ (No. 15) for the actinides (0.6%) and for $P6_3/m$ (No. 176) for the lanthanides (0.3%). Although these differences are small (vide infra) only the corrected data will be used from this point on, since the latter will be less biased.

90% of the organo-lanthanides and 91.6% of the organo-actinides fall in space groups of orthorhombic or lower symmetry. Most of the compounds have been assigned to a relatively small number of space groups. In fact, two-thirds of the compounds have been described in only three space groups: 34.1% of the lanthanides in $P2_1/c$ (actinides: 38.5%), 22.1% (20.5%) in $P\bar{1}$ and 8.3% (9.0%) in $C2/c$.

The highest difference in frequency (over 2%) of a crystal family between the two data sets occurs in the hexagonal family: 2.7% for the lanthanides compared to 0.6% for the actinides. This difference can be fully ascribed to the relatively high number of lanthanides crystallizing in space group $P6_3/m$ (No. 176), which can be explained by the crystal structure determination of two series of isomorphous compounds: one of nonaaqua lanthanide(III) tris(trifluoromethanesulfonate) compounds by Chatterjee et al. [19] and one of nonaaqua lanthanide tris(ethylsulfate) compounds by Gerkin and Reppart [20]. In order to decide whether a difference in frequency within a space group or a crystal family between the lanthanides and the actinides, or between these two and the organic compounds, is significant, a value of 2% should thus disable the bias of results due to higher interest in a given type of compounds by a certain research group.

4.2. Comparison with the data of Mighell et al.

The relative occurrences for all organic compounds according to the study by Mighell et al. [1] have been calculated and are given in the last column of Table 1.

A note should be made of the fact that, in the study of Mighell et al. [1], 195 of the 230 space groups were occupied, and that 117 space groups had five or fewer entries. Of the latter, 29 had only one entry and 35 no entry at all.

Organo-lanthanides and organo-actinides have a somewhat higher tendency to crystallize in space groups of tetragonal or higher symmetry (10.0% for lanthanides, 8.4% for actinides vs. 5.7% for organic compounds). More important is the fact that lanthanides and actinides tend to crystallize more in the triclinic crystal family than the organic compounds (22.6% for lanthanides and 21.0% for actinides vs. 14.8% for organic compounds) and less in the orthorhombic crystal family (15.4% for lanthanides and 17.0% for actinides vs. 25.8% for organic compounds). This is also reflected in the respective space groups: the number of compounds crystallizing in the triclinic space group $P\bar{1}$ (No. 2) has increased significantly, whereas the number of compounds crystallizing in the orthorhombic space group $P2_12_12_1$ (No. 19) and in the monoclinic space group $P2_1$ (No. 4) has decreased significantly. As a consequence of the decrease of the latter two, space group *C*2/*c* (No. 15) has become the third most occcupied space group in the organo-lanthanide and -actinide compounds. In the frequency table of Mighell et al. [1] *C*2/*c* was only the fifth highest occupied space group after $P2_12_12_1$ and $P2_1$.

4.3. Influence of the doubling of the number of entries crystallizing in enantiomorphic space groups

In 1985 Donohue [2] revised the space-group frequencies in the work of Mighell et al. [1] for those space groups that do not contain any operations of the second kind (inversion center or mirror planes), based on the assumption that, because the work was concerned with organic crystals, all of the crystals which were found to have (for example) space group $P2_1$ will have a corresponding enantiomer with the same space group, so the frequency should be doubled. The same situation will occur for the other 64 enantiomorphic space groups. In the case of the eleven enantiomeric pairs, for example $P3_1$ (No. 144) and $P3_2$ (No. 145), for which for the lanthanides one crystal was found in each space group, the results should be combined, to give two for each of that pair. If the enantiomorphic space group contained no entries, an extra line has been entered in Table 1 in italic type. The results of this doubling is given in the column marked "D" in Table 1 and the relative frequencies have also been calculated.

In the case of Donohue's work [2], the doubling of the frequencies for the enantiomorphic space groups had an important consequence: in combination with the evident decrease of the frequencies of the 165 non-enantiomorphic space groups, $P2_12_12_1$ (No. 19: 18.8%) now became the second most occupied space group after $P2_1/c$ (No. 14: 29.2%) but before $P\bar{1}$ (No. 2: 11.1%). In the work of Mighell et al. [1], space groups $P2_1$ (No. 4) and *C*2/*c* (No. 15) had approximately the same abundancy, whereas in Donohue's study [2] the former showed a frequency which was twice the value of the latter (10.9 vs. 5.4%). The frequencies of the eleven most occupied space groups for lanthanides and actinides are given in descending order of the corrected values of the lanthanides in Table 2. The frequencies corrected for enantiomorphism and the data for all organic compounds are also tabulated.

Whereas for the organic compounds the influence of enantiomorphism is already reversing the order of the second and third highest occupied space groups ($P\bar{1}$ and $P2_12_12_1$ respectively), there is only a change in order observed between the fifth and the sixth most occupied space group among the actinides (*Pbca* and $P2_1$ respectively). The influence may even be neglected for the lanthanides. This might be explained by the fact that lanthanide and actinide compounds crystallize significantly less in enantiomorphic and more in centrosymmetric space groups than when all organic compounds are taken into consideration [1], so the effect of doubling the number of compounds crystallizing in enantiomorphic space groups is less important for this type of compound.

4.4. Division of the data into type of space group

Space groups can be divided into different types. The type(s) to which a given space group belongs has (have) been indicated by an asterisk in columns 3 to 5 in Table 1.

Only 11.5% of the lanthanide and 10.1% of the actinide compounds crystallize in one of the 65 enantiomorphic space groups. These numbers are significantly smaller compared with the 23.1% for all organic compounds which have been calculated from the paper by Mighell et al. [1]. These numbers agree with the number of compounds crystallizing in one of the 93 centrosymmetric space groups: 78.5% for the lanthanides and 81.7% for the actinides vs. 70.4% for all organic compounds.

The number of compounds crystallizing in one of the 73 symmorphic space groups is also higher than the 18.6% calculated for all organic compounds; 27.9% and 24.7% for the lanthanides and actinides respectively. This agrees with the fact that the number of compounds crystallizing in the triclinic family is higher for the latter two.

4.5. Occupation of special positions

A set of symmetrically equivalent points (e.g. atoms) is said to be in "special position" if each of its points is mapped onto itself by at least one further symmetry operation of the space group, for example a mirror plane or an inversion center. If the number of molecules in the unit cell (ZVAL) is smaller than the multiplicity, which is defined as the number of equivalent points, then the molecules lie on a special position. A space group may have several special positions depending on the number and type of symmetry operations.

Upon analysis of the data it was observed that 34.1% of the lanthanides and 38.1% of the actinides crystallized in such a way that their molecules are in a special position. In fact, for space groups of tetragonal or higher symmetry this is more the rule (80% or more) than the exception.

In Table 3 the percentages are given for the organo-lanthanides and -actinides which have more than ten entries and which crystallize in such a way that the molecules occupy special positions for space groups of orthorhombic symmetry or lower. For comparison, the corresponding numbers for all organic compounds have been determined from the CSD. It can be observed that, with exception of space groups 2 and 14 for the

Table 2
Frequencies of the eleven most occupied space groups, in descending order of the corrected values for the lanthanide compounds

SPGN	SPAC	Lanthanides		Actinides		Organic	
		C (%)	*D* (%)	*C* (%)	*D* (%)	*C* (%)	*D* (%)
14	$P2_a/c$	34.1	30.6	38.5	34.9	36.0	29.2
2	$P\bar{1}$	22.1	19.8	20.5	18.7	13.7	11.1
15	$C2/c$	8.3	7.4	9.0	8.3	6.6	5.4
4	$P2_1$	3.8	6.9	2.3	4.2	6.7	10.9
19	$P2_12_12_1$	3.7	6.6	3.9	7.2	11.6	18.8
61	*Pbca*	2.4	2.2	2.8	2.6	4.3	3.5
33	$Pna2_1$	2.3	2.1	1.5	1.3	1.8	1.4
60	*Pbcn*	2.0	2.0	1.2	1.1	1.2	1.0
62	*Pnma*	1.3	1.1	2.3	2.1	1.9	1.5
5	*C2*	0.8	1.5	0.2	0.4	0.9	1.5
1	*P1*	0.5	0.9	0.5	0.9	1.0	1.7

Table 3
Percentage of compounds crystallizing with their molecules in special positions

SPGN	Lanthanides	Actinides	Organic
2	20.6	30.5	20.1
14	15.8	22.8	15.9
15	73.7	78.4	54.5
60	75.0	60.0	62.0
61	20.0	39.1	13.4
62	100.0	94.7	92.8

organo-lanthanides, the percentages of the compounds discussed here are significantly higher than for all organic compounds. From this it follows that organo-lanthanides and -actinides show a higher tendency to retain the inherent molecular symmetry in a crystal without a material loss in packing density [21].

4.6. *Compounds crystallizing with more than one molecule in the asymmetric unit*

It can also occur that the number of molecules in the unit cell (ZVAL) is larger than the multiplicity of the space group. In this case there will be two or more crystallographically independent molecules in the asymmetric unit.

5.6% of the lanthanides and 3.9% of the actinides have more than one molecule in the unit cell. This feature mainly occurs within the triclinic and monoclinic families, and in a few cases only in the orthorhombic family. No examples have been found in space groups of tetragonal or higher symmetry.

5. Conclusion

The number of space groups in which organo-lanthanides and -actinides crystallize is smaller than for all organic compounds. This is not necessarily a specific feature observed for this type of compounds, but may also be the result of the fact that both data sets are smaller than the one used by Mighell et al. [1].

The influence of removing double entries is small. It may be argued that entries of space groups not substantiated by a complete structure determination (i.e. COOR = 0), or dubious because of disorder in the crystal, should not be selected for this type of study. This has been done in the recent studies by Padmaja et al. [6] and Wilson [5]. However, in both studies all duplicates were eliminated on the basis of the CSD refcode, consequently also deleting different modifications (which might crystallize in the same or a different space group) of compounds having identical refcodes.

The distribution of crystalline organo-lanthanides and -actinides is fairly similar. Compared with all organic compounds, the lanthanide and actinide compounds show a somewhat higher tendency to crystallize in space groups of tetragonal or higher symmetry. The trend to crystallize more in the triclinic than in the orthorhombic crystal family or to crystallize more in centrosymmetric than in non-centrosymmetric space groups is quite clear.

This study was undertaken without a prior knowledge of the inherent molecular symmetry of the molecules taken into consideration. The molecular symmetry in the crystal is in general lower than the inherent molecular symmetry [21]. Compounds which crystallize in space groups $P2_1$ or $P2_12_12_1$ (respectively Nos. 4 and 19) have no molecular symmetry (i.e. only the trivial symmetry 1), which corresponds to an inherent molecular symmetry 1 or 2. On the other hand, the compounds which crystallize in space group $C2/c$ (No. 15) have a molecular symmetry $\bar{1}$ or 2, which corresponds to an inherent molecular symmetry $\bar{1}$, $2/m$, 222 or *mmm* [21]. Since the number of organo-lanthanide and actinide compounds which crystallize in space group $C2/c'$ was higher and the number which crystallize in space groups $P2_1$ or $P2_12_12_1'$ was lower than for the organic compounds, this indicates that the inherent molecular symmetry of the compounds of the present study is higher than for organic compounds as a whole. Moreover, the higher tendency to crystallize in space groups of tetragonal or higher symmetry, combined with the fact that more than 80% of the molecules in these crystal families occupy special positions, gives another indication that organo-lanthanides and -actinides have a higher inherent molecular symmetry than organic compounds in general.

Since the f electrons in organometallic compounds are relatively uninvolved in bonding, to a lesser degree in the lanthanides even than in the actinides, no conclusion can be drawn about the differences in electronic structure for the compounds under study compared with compounds having no f electrons. From the point of view of crystal engineering, the fact that organo-lanthanides and -actinides tend to crystallize more in centrosymmetric space groups than all organic compounds is important. Indeed, for a number of physical properties, such as pyroelectricity, piezoelectricity or non-linear optical activity, the absence of a center of symmetry is a prerequisite.

6. Note on the study by Padmaja et al.

Within their study on the space-group frequencies of proteins and of organic compounds with more than one formula unit in the asymmetric unit, Padmaja et al. [6] also included a table for 51 611 organic compounds reported up to 1987. The data are comparable with those of Mighell et al. [1], and the number of occupied space groups has increased to 202. With the exception of one space group, the changes in frequency are in the order of a few tenths of one percent: for $P\bar{1}$ there is a significant increase by 3.1%.

With respect to the present study, the following data of Padmaja et al. [6] are of interest: 95.4% of all organic compounds crystallize in space groups of orthorhombic or lower symmetry: 18.1% in the triclinic and 23.4% in the orthorhombic family. According to the different types of space groups, the following numbers have been calculated: 21.9% crystallize in enantiomorphic, 72.4% in centrosymmetric and 21.1% in symmorphic space groups. In none of these cases are the numbers in conflict with the conclusions of the present study.

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