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The crystal structure of cerium *tetrakis*-dibenzoylmethane.

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The aromatic coordination compounds of uranium and thorium are of interest because they have a high solubility in organic moderators and are reported to have high thermal and radiation stability as reported by Comyns (1957). They thus fulfil an essential requirement of suitability for use as fuel in homogeneous organic reactors. Dibenzoylmethane C_6H_5–CO–CH_2–CO–C_6H_5 is one of the simplest aromatic chelating agents and combines with uranium, thorium and cerium to give complexes which closely resemble organic compounds in some of their properties. Wolf (1957) has shown that those complexes are isomorphous with each other and therefore the cerium complex is chosen as representative for structure analysis. Of the three, cerium is the lightest metal and will therefore cause the least severe diffraction effects in the Fourier analysis.

Experimental

Wolf (1957) has reported the space group and the values of the cell dimensions of the complexes of uranium, thorium and cerium. The values for the cerium complex are

$$a=20\cdot109,\quad b=10\cdot320,\quad c=23\cdot514\ \text{Å};$$
$$Z=4,\quad d_c=1\cdot52\ \text{g.cm.}^{-3},\quad d_o=1\cdot52\ \text{g.cm.}^{-3}.$$
$$\text{Space group: } Pccn\,.$$

Wait & Comyns (1958) have reported the values for the thorium compound. They are nearly the same as those given by Wolf (1957).

The cerium complex was recrystallized from toluene. The linear absorption coefficient of this compound for Cu $K\alpha$ radiation was calculated and found to be small (90 cm.$^{-1}$). For crystals of 0·02 cm. in diameter no absorption correction was therefore necessary. The data were collected from the Weissenberg photographs round the b axis. The multifilm technique was used and the intensities were measured visually by comparison with a calibration strip and corrected for the Lorentz and polarization factors.

Structure analysis

The best resolved projection—that on (010)—was adopted for the structure analysis. The four cerium atoms in the unit cell have to occupy one of the four-fold positions (*d*), (*c*), (*b*) or (*a*). A survey of the intensities of the reflections shows that *hkl* with $l=2n+1$ are weak. Thus the cerium has to occupy either (*d*) or (*c*).

$$(d)\quad \tfrac{1}{4},\tfrac{3}{4},z;\ \ \tfrac{3}{4},\tfrac{1}{4},\bar{z};\ \ \tfrac{1}{4},\tfrac{3}{4},\tfrac{1}{2}+z;\ \ \tfrac{3}{4},\tfrac{1}{4},\tfrac{1}{2}-z\,,$$
$$(e)\quad \tfrac{1}{4},\tfrac{1}{4},z;\ \ \tfrac{3}{4},\tfrac{3}{4},\bar{z};\ \ \tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{2}+z;\ \ \tfrac{3}{4},\tfrac{3}{4},\tfrac{1}{2}-z\,.$$

Both these two positions have a two-fold point symmetry and differ only in the choice of origin. In the (010) projection these two positions are identical.

The x coordinate of the cerium atom is fixed by the space group and the value of the z coordinate is derived from the Patterson synthesis. This gives two possible values 0·137 and 0·113 (expressed in terms of the fractional coordinates) for z. Two separate Fourier syntheses were made by taking the signs by the two sets of coordinates. The value of $z=0\cdot137$ was discarded because the resulting synthesis yielded a structure which gave a high value for the agreement index and this could not be improved even after making large shifts in the positions of the atoms.

For interpreting the syntheses resulting from $z=0\cdot113$ a wire model of the structure was built on the assumption that the coordination of the eight oxygen atoms round the cerium has a square antiprismatic configuration. The value for the bond-length Ce–O was taken as 2·31 Å and the angle O_1–Ce–O'_1 was taken to be 70° from the known structure of cerium iodate by Cromer & Larson (1956). The shadow of this model was cast on the electron-density map for locating the light atoms.

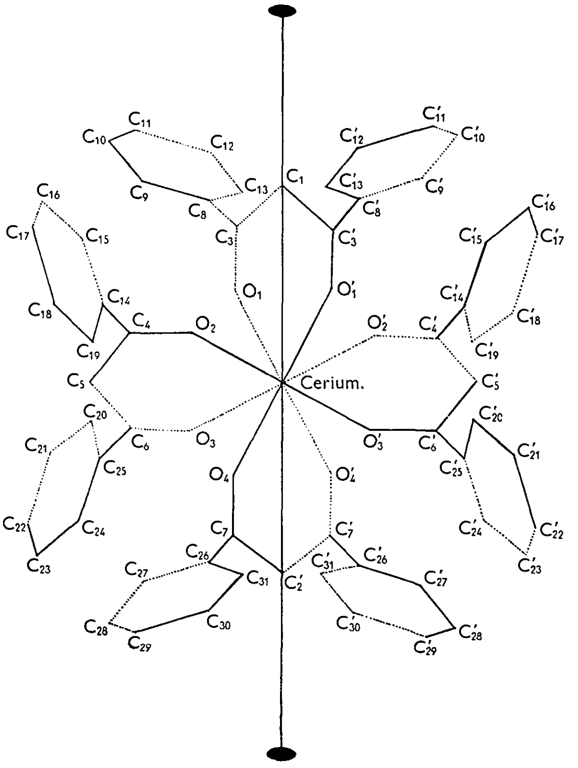

Fig. 1. A schematic drawing of the molecule with all the atoms labelled.

Fig. 1 shows the model of the molecule with all the atoms labelled. The two-fold axis of symmetry of the molecule passes through C_1, Ce, C_2. The plane containing the atoms $O_1CeO'_1$ makes an angle of 45° with the plane which contains the atoms O_4, Ce, O'_4. Similarly the plane containing O_2, Ce, O'_3 makes an angle of 45° with the plane which contains O_2CeO_3.

The agreement index R for this projection is 0·26.

The lighter carbon and oxygen atoms have a very small contribution to the higher-order reflections, and the Fourier synthesis does not give accurate coordinates for these atoms. Further three-dimensional work is therefore planned. The other two projections are badly resolved and are not suitable for further structure analysis.

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X-ray studies of molecular overcrowding. I. Some crystallographic data.

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With a view to obtaining detailed information about the effect on the molecular geometry of the close approach of neighbouring groups structural analysis of a number of substituted benzoic acids is at present in progress. As a preliminary to this work lattice parameters and space groups were determined and are presented in Table 1. In the case of *o*-chlorobenzoic acid and *o*-bromobenzoic acid the diffraction conditions allow the space group to be either $Cc\text{–}C_s^4$ or $C2/c\text{–}C_{2h}^6$. The successful refinement of the structure based on the centrosymmetrical choice indicates $C2/c$ as the true space group.

Full details of the structure determinations will be published in due course.

Table 1. *Crystallographic data for some substituted benzoic acids*

	o-chlorobenzoic acid	*o*-bromobenzoic acid	2-chloro-5-nitro-benzoic acid	4-chloro-3-nitro-benzoic acid
Molecular formulae	$C_7H_5O_2Cl$	$C_7H_5O_2Br$	$C_7H_4O_4NCl$	$C_7H_4O_4NCl$
a (Å)	14·73 ± 0·03	14·82 ± 0·04	5·86 ± 0·02	7·41 ± 0·02
b (Å)	3·90 ± 0·02	4·10 ± 0·02	5·13 ± 0·02	5·70 ± 0·02
c (Å)	25·50 ± 0·05	25·90 ± 0·05	26·65 ± 0·05	19·12 ± 0·04
β	112° 40′	118° 15′	97° 54′	100° 30′
U (Å^3)	1351	1386	794	794
z	8	8	4	4
Mol.wt.	156·6	201·0	201·6	201·6
D_m (g.cm.$^{-3}$)	1·544	1·929	1·678	1·687
D_x (g.cm.$^{-3}$)	1·539	1·926	1·687	1·686
Space group	$C2/c\text{–}C_{2h}^6$	$C2/c\text{–}C_{2h}^6$	$P2_1/c\text{–}C_{2h}^5$	$P2_1/c\text{–}C_{2h}^5$

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Unit cell and space group of L-proline monohydrate.

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Crystals of L-proline are highly hygroscopic. Therefore there has been considerable difficulty in growing single crystals suitable for X-ray diffraction studies. When grown from a saturated solution in a closed container, the crystals occur as a white powder or take up a featherlike formation, but no large enough single crystals appear at room temperature. The powder pattern obtained from this material was found to be very much different from that of the original compound thereby showing that the compound was a hydrated form of proline. The unit-cell dimensions and space group of the original dry powder have already been reported (Wright & Cole, 1949). Successful single crystals of the hydrated compound were grown by the author from a solution of the dry material in ethyl alcohol by controlling the percentage of alcohol and the temperature at which the compound was crystallised. Single crystals of the monohydrate were obtained by dissolving the substance in 70% ethanol and keeping the solution at a constant temperature of 45 °C.

The crystals obtained were needle-shaped, transparent, birefringent and approximately rectangular in cross section. The needles were elongated along [001] and bounded by faces of the form {110}. As the crystals were unstable when exposed to the atmosphere, considerable care was taken to protect the crystals by enclosing them in Lindemann-glass tubes at 45 °C. Even then the crystals were stable for only a few days.