[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY, UNIVERSITY OF CALIFORNIA, LOS ALAMOS]

The Crystal Structure of [(CH₃)₄N]₂CeCl₆[1]

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$[(CH_3)_4N]_2CeCl_6$ has the R_2MX_6 fluorite-type structure with $a_0 = 13.05$ Å. It is isomorphous with the analogous tin and platinum compounds. Analysis of X-ray powder diffraction data leads to the value 2.55 Å. for the Ce–Cl distance.

Introduction

It was of interest to this Laboratory to know the cerium–chlorine distance in the compound $[(CH_3)_4N]_2CeCl_6$. The structures of the analogous tin and platinum compounds have been reported by Wyckoff and Corey,[2] and by Huggins.[3] In this work it was assumed that the cerium compound is isomorphous with the tin and platinum compounds and that the space group is Fm3m–O_h^5.[5] Since the agreement between calculated and observed intensities is satisfactory, these assumptions are justified. Many structures of this type have been summarized by Wyckoff,[4] but no cerium compounds have been reported. Some properties of related compounds have been given by Staritzky and Singer.[5]

TABLE I

INTENSITY DATA FOR [(CH₃)₄N]₂CeCl₆

Miller index followed by w_i', G_i^2(obsd.) $\times 10^{-4}$, and G_i^2(calcd.) $\times 10^{-4}$ in order: 111 (5) (68) (82); 200 (8) (18) (22); 220 (8) (58) (66); 311 (8) (52) (73); 222 (6) (14) (16); 400 (8) (82) (100); 420 (6) (82) (60); 422 (6) (14) (12); 511, 333 (8) (130) (153); 440 (8) (68) (74); 531, 600, 442 (8) (226) (217); 620 (8) (62) (55); 533, 622 (3) (12) (8); 444 (4) (26) (19); 711, 551, 640 (7) (244) (197); 642 (5) (70) (54); 731, 553 (5) (109) (83); 733, 820, 644 (4) (60) (39); 822, 660 (6) (42) (44); 751, 555, 662 (7) (108) (86); 840 (2) (11) (21); 911, 753, 842 (4) (55) (31); 664 (2) (23) (32); 931 (2) (20) (10); 933, 755, 771, 860, 1000 (2) (52) (51); 1020, 862 (2) (30) (25); 951, 773, 1022, 666 (2) (45) (53); 953, 1040, 864 (2) (48) (39); 1042 (2) (10) (19); 1111, 775 (1) (7) (16); 1131, 971, 955, 1044, 882 (1) (70) (51).

Experimental

The compound was prepared by adding, at 0°, 0.5 M Ce(ClO₄)₄ in 6 M HClO₄ to concentrated HCl which contained the stoichiometric amount of (CH₃)₄NCl. X-Ray powder photographs of the product were indexed on the basis of a face-centered-cubic lattice with $a_0 = 13.05 \pm 0.03$ Å. The photographs were nearly identical with powder photographs of $[(CH_3)_4N]_2UCl_6$. Since the latter compound is well-known,[6] the similarity of the powder photographs was taken as proof of the identity of the cerium compound. There were a few lines present which were from some unidentified impurity. The spurious lines from one preparation were spotted while the desired lines were smooth. This observation established that the spurious lines were indeed from some impurity and not from the material being studied.

(1) This work was performed under the auspices of the Atomic Energy Commission.

(2) R. W. G. Wyckoff and R. B. Corey, Am. J. Sci., [5] 18, 437 (1929).

(3) M. L. Huggins, Phys. Rev., 27, 638 (1926).

(4) R. W. G. Wyckoff, "Crystal Structures," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1951.

(5) E. Staritzky and J. Singer, Acta Cryst., 5, 536 (1952).

(6) G. H. Dieke and A. B. F. Duncan, "Spectroscopic Properties of Uranium Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

Powder photographs for various exposure times were taken with nickel-filtered copper radiation. The integrated intensities of most of the lines were measured with a Leeds and Northrup recording densitometer. The intensities of the weaker lines were visually estimated. The intensities of some of the lines were also obtained with a General Electric XRD-3 X-ray diffractometer. The intensities from the powder photographs were corrected for absorption in the usual way for cylindrical samples.[7] For this purpose the bulk density of the sample was assumed to be 40% of the true density. μR was 1.1, resulting in an almost negligible absorption correction in the range of θ experimentally obtained. The material in the capillary was later weighed. From the measured volume of the sample and the weight of the sample, the bulk density was calculated to be 57% of the true density. μR was therefore 1.6 instead of 1.1, the value used in making the absorption correction. The small error introduced here probably results primarily in a slightly erroneous temperature factor.

As a matter of interest, the refractive index of $[(CH_3)_4N]_2$-CeCl₆ for sodium light was measured and found to be 1.544 ± 0.001.

Determination of the Structure.—Atoms were assigned to the following positions of space group Fm3m

$\quad$ 4 Ce in (a): 000 + F.C.

$\quad$ 8 N in (c): $\pm(^1/_4, \,^1/_4, \,^1/_4)$ + F.C.

$\quad$ 24 Cl in (e): $\pm(X00; \, 0X0; \, 00X)$ + F.C.

$\quad$ 32 C in (f): $\pm(XXX; \, X\overline{XX}; \, \overline{X}X\overline{X}; \, \overline{XX}X)$ + F. C.

Neglecting the hydrogen atoms there are two parameters in the structure, one for the chlorine atom and one for the carbon atom. These two parameters were first estimated from known atomic sizes and then refined by the method of least squares.[8] Since many of the lines were composite, the refinement could not be made with respect to the structure factors. Instead, the refinement was made with respect to the quantities ΔG_i^2 defined as[9]

$$G_i^2 \text{ (calcd.)} = t_i^2 \sum_j m_j F_j^2 \text{ (calcd.)} \qquad (1)$$

$$G_i^2 \text{ (obsd.)} = I_i \text{(obsd.)}/kLP \qquad (2)$$

$$\Delta G_i^2 = G_i^2 \text{ (obsd.)} - G_i^2 \text{ (calcd.)} \qquad (3)$$

where

$$t_i^2 = \exp\left(-B \sin^2\theta_i/\lambda^2\right) \qquad (4)$$

is the temperature factor, m_j is the multiplicity of the jth form present in the ith line, LP is the Lorentz polarization factor and k is the scale factor. The observational equations were of the form

$$\sqrt{w_i} \, \frac{\partial G_i^2(\text{calcd.})}{\partial x_1} \Delta x_1 + \sqrt{w_i} \, \frac{\partial G_i^2(\text{calcd.})}{\partial x_2} \Delta x_2 = \sqrt{w_i} \Delta G_i^2 \qquad (5)$$

where x_1 is the chlorine parameter, x_2 is the carbon parameter and $w_i = w_i'/[G_i^2(\text{obsd.})]^2$ is the weighting factor. w_i' is an auxiliary weight ranging from 1 to 8 depending on what we believed to be the

(7) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Vol. II, Borntraeger, Berlin, 1935.

(8) E. Hughes, THIS JOURNAL, 63, 1737 (1941).

(9) D. Shoemaker, et al., Acta Cryst., 5, 637 (1952).

validity of the intensity measurement. It was highest for well-defined lines measured with the densitometer and diffractometer and lowest for the broader and weaker lines which were visually estimated. Scale and temperature factors were obtained from the least-squares solution of the semilog plot of $G_i{}^2$(obsd.)$/G_i{}^2$ (calcd.) vs. $\sin^2\theta/\lambda^2$. The value 5.43 Å.[2] was ultimately obtained for B.

Thirty-one observational equations were used and reduced in the usual way to two normal equations which were solved for x_1 and x_2. The 331 and 800 lines were omitted because of uncertainty in the signs of their structure factors. Atom form factors were taken from "Internationale Tabellen."[7] The form factor for cerium(IV) was approximated by the expression

$$f_{Ce(IV)} = \frac{54}{58} f_{Ce}$$

The final values for the parameters are

$$x_1 = 0.1951 \pm 0.0008$$
$$x_2 = 0.3119 \pm 0.0014$$

The uncertainties are standard deviations calculated according to Wittaker and Robinson.[10] The interatomic distances are therefore

(10) E. Wittaker and G. Robinson, "The Calculus of Observations," 4th Edition, Blackie and Son, London, 1944, Chapter 9.

$$Ce-Cl = 2.55 \pm 0.01 \text{ Å.}$$
$$C-N = 1.40 \pm 0.03 \text{ Å.}$$
$$CH_3-Cl = 3.79 \pm 0.05 \text{ Å.}$$

The error given here is believed to be somewhat low since no account of systematic errors has been taken in the statistical treatment.

Subtracting 0.99 Å., the covalent radius of chlorine, from the cerium–chlorine distance gives the value 1.56 Å. for the octahedral radius of cerium.[11] The carbon–nitrogen distance is significantly shorter than 1.47 Å., the sum of the covalent radii.[11] A shortening of this bond is expected because of the positive charge on the nitrogen atom. In any event, short carbon–nitrogen bonds are by no means unusual.[12] The sum of the van der Waals radii for chlorine and a methyl group is 3.80 Å.,[11] in excellent agreement with the value given above for the distance from methyl group to chlorine atom.

Observed and calculated values of $G_i{}^2$ are given in Table I. The discrepancy factor, $R = \Sigma |\Delta G_i{}^2| / \Sigma |G_i{}^2\text{(obsd.)}|$, is 21%. If computed on the basis of structure factors, as is usually done, R would be about half as great.[9]

(11) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948.
(12) C. Brown, Acta Cryst., 2, 228 (1949).

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The Crystal Structure of Sodium Oxalate

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Sodium oxalate has a simple type of ionic structure with a distorted octahedral coördination of oxygen atoms around the sodium ions. The space group is P2₁/a with two Na₂(COO)₂ in a unit cell of dimensions $a = 10.35$, $b = 5.26$, $c = 3.46$ Å., all ± 0.02 Å., $\beta = 92°54 \pm 6'$. The crystal structure was determined from the ($h0l$) and ($hk0$) intensities and the atomic parameters were refined by Fourier projections and difference syntheses on (010) and (001). The dimensions of the oxalate ion, C–C = 1.54 Å., C–O = 1.23 Å., C–C–O 121° and 115°, O–C–O 124°, are in good agreement within experimental errors with those determined in ammonium oxalate hydrate. The oxalate ion in the sodium salt is planar, in contrast to that in the ammonium oxalate hydrate, and it is concluded that this difference in stereochemistry is a consequence of the hydrogen bond structure in the latter.

The difference in configuration between the nonplanar oxalate ion found in $(NH_4)_2(COO)_2 \cdot H_2O$[3] and the planar acid molecule in $\alpha\text{-}(COOH)_2$,[4] $\beta\text{-}(COOH)_2$,[5] $(COOH)_2 \cdot 2H_2O$,[6] raises the question as to whether this is a characteristic difference between the ion and the acid molecules or a consequence of interionic or intermolecular forces in the crystal structures. An examination of the reported data on oxalate structure does not provide a conclusive answer. The crystal structures of the isomorphous $K_2(COO)_2 \cdot H_2O$ and $Rb_2(COO)_2 \cdot H_2O$ were studied by Hendricks,[5] who reported the crystallo-

(1) Department of Chemistry, University of Pittsburgh.
(2) Scaife Foundation Fellow, University of Pittsburgh.
(3) G. A. Jeffrey and G. S. Parry, J. Chem. Soc., 4864 (1952); S. Hendricks and M. E. Jefferson, J. Chem. Phys., 4, 102 (1936).
(4) E. G. Cox, M. W. Dougill and G. A. Jeffrey, J. Chem. Soc., 4854 (1952).
(5) S. Hendricks, Z. Krist., 91, 48 (1935).
(6) D. W. J. Cruickshank and F. R. Ahmed, Acta Cryst., 6, 385 (1953).

graphic data included in Table I. If the space group of these compounds in C2/c, the oxalate ion must be centrosymmetrical and with the assumption of planar trigonal carbon valences, the whole ion must be planar. However the space group C2/c is not uniquely determined and the alternative Cc symmetry must be eliminated by the results of the structure analysis. Hendricks' early analysis was based on qualitative intensity estimations of 37 reflections, and it would appear from the published record that not very good agreement was obtained between observed and calculated intensities. The dimensions found for the oxalate ion, C–C = 1.60 Å., and unequal C–O bonds 1.14 Å., and 1.30 Å., suggest ill-defined atom positions, at least for the anions. Although the cations may be approximately arranged according to the space group C2/c, there is no evidence that this is necessarily true for the oxalate ions and water molecules and the space group assignment must be regarded as inconclusive.