

References

- ČELAP, M. B., MALINAR, M. J. & JANJIĆ, T. J. (1974). XVIII Annual Meeting of the Serbian Chemical Society, *Bull. Soc. Chim. Beograd*, **39**, 168.
- CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- FREEMAN, H. C. (1967). *Advanc. Protein Chem.* **22**, 257.
- HERAK, R. & PRELESNIK, B. (1973). *Proc. Fourth Conf. Coordination Chemistry, The Second Seminar of Crystallochemistry of Coordination and Metallorganic Compounds*, Smolenice-Bratislava, CSSR, 1973, p. 35..
- HERAK, R., PRELESNIK, B., MANOJLOVIĆ-MUIR, L. & MUIR, K. W. (1974). *Acta Cryst.* **B30**, 229–231.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202–207. Birmingham: Kynoch Press.
- KENT MURMANN, R. & SCHLEMPER, E. O. (1973). *Inorg. Chem.* **12**, 2625–2631.
- OONISHI, I., FUJIMAKI, H., MUTO, F. & KOMIYAMA, Y. (1970). *J. Chem. Soc. Japan*, **43**, 733–739.
- SVETICH, G. W., VOGEL, A. A., BRUSHMILLER, J. G. & BERENDS, E. A. (1972). *Chem. Commun.* p. 701.
- WATSON, W. H., JOHNSON, D. R., ČELAP, M. B. & KAMBERI, B. (1972). *Inorg. Chim. Acta*, **6**, 591–597.

Acta Cryst. (1976). **B32**, 94

A Powder Neutron Diffraction Study of Lanthanum and Cerium Trifluorides

BY A.K. CHEETHAM AND B.E.F. FENDER

Inorganic Chemistry Department, University of Oxford, England

AND H. FUESS AND A.F. WRIGHT

Institut Laue-Langevin, B.P. 156, 38042 Grenoble Cedex, France

(Received 24 May 1975; accepted 28 May 1975)

The structures of LaF_3 and CeF_3 have been re-examined by neutron powder diffraction by the profile analysis method in order to decide between the three space groups proposed for the tysonite structure ($P\bar{3}c1$, $P6_3/mcm$ and $P6_3mc$). The refinement of positional and thermal parameters gave strong support for $P\bar{3}c1$. The rare-earth atoms have an 11-fold coordination of F atoms with distances between 2.421 and 2.999 Å (LaF_3) and 2.400 and 2.974 Å (CeF_3). It is shown that a high intensity/low resolution instrument gives results equivalent to those from a high resolution/medium intensity instrument.

Introduction

The trifluorides of the early lanthanides, La, Ce, Pr, Nd, adopt the structure of the natural mineral tysonite (a lanthanum cerium fluoride). Pure LaF_3 in particular has been extensively studied but the structure is still disputed. Single-crystal studies by Mansmann (1965) and Zalkin, Templeton & Hopkins (1966) indicate the space group $P\bar{3}c1$, a result supported by Raman measurements (Bauman & Porto, 1967). On the other hand the X-ray and neutron measurements of de Rango, Tsoucaris & Zelwer (1966) have been interpreted in $P6_3cm$, while from recent *n.m.r.* results on CeF_3 , PrF_3 and NdF_3 Afanasiev, Habuda & Lundin (1972) favour $P6_3/mcm$ (the same space group is implied for LaF_3). The alternatives are summarized in Table 1.

We have re-examined the structure of LaF_3 by neutron diffraction because of its importance as a host crystal for the spectroscopic investigation of paramagnetic lanthanide ions, with particular relevance to crystal-field calculations (*e.g.* Newman & Curtis, 1969). Results for CeF_3 are also presented. Finally, as part of a programme to assess the value of profile analysis techniques, we compare the merits of the LaF_3

data which were collected on an instrument with modest resolution and a restricted angular 2θ range but high intensity, with the CeF_3 data collected on a high-resolution diffractometer.

Experimental

Powder neutron diffraction experiments were carried out on LaF_3 (supplied as 'Optran' quality by BDH Ltd., England) at room temperature with the D2 diffractometer on the High Flux Beam Reactor at the ILL, Grenoble. Data were collected over a period of about 6 h from 5° to 61° (in 2θ) in steps of 0.1° . The neutron beam was monochromated by the 200 planes of a Cu crystal with a take-off angle of about 14° in 2θ . The wavelength was not determined independently, but with the Zalkin *et al.* (1966) cell parameters $a = 7.185$, $c = 7.351$ Å it was deduced to be 1.085 Å. Absorption effects were negligible and no correction was applied.

The CeF_3 was supplied from the Cerac range of materials by Cambrian Chemicals Ltd., England and the experiment was performed at room temperature on the high-resolution D1A diffractometer at the ILL. Data were collected with neutrons of mean wavelength

1.509 Å over a range of 2θ from 30° to 115° in steps of 0.05° . The neutron beam was monochromated by reflexion from the 533 planes of a Ge crystal at a take-off angle of 58° . The duration of the experiment was 85 h. Profile analysis of the diffraction pattern (see below) gave $a=7.131$ (1), $c=7.286$ (1) Å; the values reported by Zalkin & Templeton (1953) were $a=7.114$ (4), $c=7.273$ (5) Å. Again, no correction for absorption was necessary.

Results

LaF₃

$P\bar{3}c1$. The structural parameters were refined by full-matrix least-squares analysis of the powder diffraction profile (Rietveld, 1969). Despite the low resolution of the D2 instrument which was primarily conceived for magnetic structure determination, the refinement rapidly converged in $P\bar{3}c1$ starting from the parameters of Mansmann. The scattering lengths used were $b_{\text{La}}=0.83 \cdot 10^{-12}$, $b_{\text{F}}=0.565 \cdot 10^{-12}$ cm (Shull, 1972). Isotropic Debye-Waller factors were refined

for La and F with those for different F atoms constrained to be equal. The program minimizes $\chi^2 = \sum_i w_i |y_i(\text{obs}) - 1/cy_i(\text{calc})|^2$ where w_i is a weighting function, y_i the number of counts at a point i in 2θ and c is a scale factor. The final R based on profile intensities, defined as

$$R_{\text{profile}}(\text{weighted}) = 100 \frac{\sum_i w_i |y_i(\text{obs}) - 1/cy_i(\text{calc})|^2}{\sum_i w_i |y_i(\text{obs})|^2},$$

converged to 6.2% after four cycles, compared with an idealized minimum of 5% expected from purely statistical errors. The profile fit is shown in Fig. 1. The results are given in Table 2 with those of Mansmann (1965) and Zalkin *et al.* (1966). The agreement between the three sets of results is good although the coordinates of F lie somewhat outside the experimental X-ray standard deviations. As expected, the precision of the F coordinates is greater in the neutron study.

$P6_3/mcm$ and $P6_3cm$. The refinement in $P6_3/mcm$ gave $R_{\text{pr}}=19.4\%$ so that we can discount this space group. The disordered structure proposed by Afanasiev *et al.* (1972) for PrF₃ and NdF₃ was also considered and

Table 1. Proposed space groups for the tysonite structure

Space group $P\bar{3}c1$ Mansmann (1965) Zalkin <i>et al.</i> (1966)	Space group $P6_3/mcm$ Afanasiev <i>et al.</i> (1972) Ofteidal (1931)	Space group $P6_3cm$ de Rango <i>et al.</i> (1966)
6 Ln in (f) $x, 0, \frac{1}{4}$	6 Ln in (g) $x, 0, \frac{1}{4}$	6 Ln in (c) $x, 0, \frac{1}{4}$
12 F(1) in (g) x, y, z	12 F(3) in (k) $x, 0, z$	2 F(1) in (a) $0, 0, z$
4 F(2) in (d) $\frac{1}{3}, \frac{2}{3}, z$	4 F(2) in (c) $\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$	4 F(2) in (b) $\frac{1}{3}, \frac{2}{3}, z$
2 F(3) in (a) $0, 0, \frac{1}{4}$	2 F(1) in (a) $0, 0, \frac{1}{4}$	6 F(3) in (c) $x, 0, z$
		6 F(4) in (c) $x, 0, z$

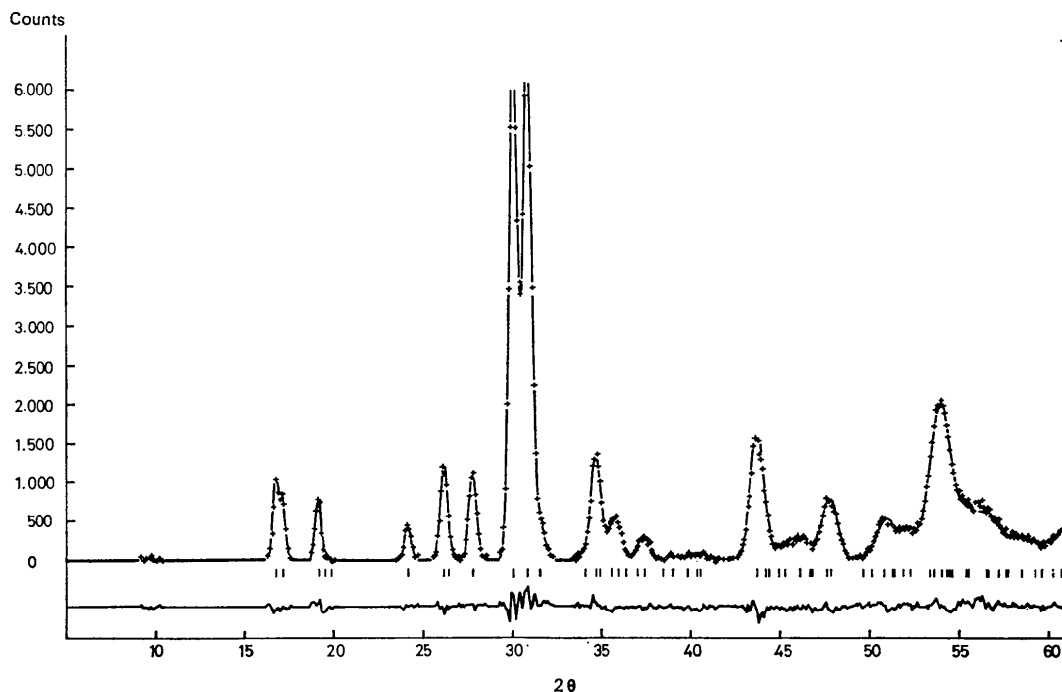


Fig. 1. Powder pattern of LaF₃ obtained on the low-resolution instrument D2 ($\lambda=1.085$ Å): + observed intensity; - calculated intensity. The difference between observed and calculated intensities is given below.

found to be unsatisfactory. However a refinement based on $P6_3cm$ proposed by de Rango *et al.* (1966) and their published positional and thermal parameters yielded a good fit ($R_{pr} = 6.3\%$) so that our powder diffraction study does not in itself discriminate between $P\bar{3}c1$ and $P6_3cm$. However, the centrosymmetric space group would normally be preferred since it gives a comparable fit with only five variable atomic coordinates against seven in $P6_3cm$.

In addition all the indirect evidence points to the centrosymmetric space group. There is neither a pyro- (Zalkin *et al.*, 1966) nor a piezoelectric effect

(Mansmann, 1965) while the n.m.r. evidence, though failing to detect the lower symmetry of the structure, indicates *three* different F atoms rather than *four* as required by $P6_3cm$.

CeF₃

Least-squares refinements by profile methods were again carried out in $P\bar{3}c1$, $P6_3/mcm$ and $P6_3cm$; the final weighted R 's were 12.81, 39.4 and 12.59% respectively. The expected R on the basis of counting statistics was 10.14%. The higher R 's compared with LaF₃ are due to the lower counting statistics on the high-

Table 2. Atomic coordinates and temperature factors for LaF₃ and CeF₃

Atom	Present work LaF ₃	Mansmann (1965) LaF ₃	Zalkin <i>et al.</i> (1966) LaF ₃	Present work CeF ₃
Ln/Ce				
x	0.6609 (10)	0.6587 (2)	0.6599 (5)	0.6607 (7)
$B[\text{\AA}^2]$	0.24 (6)	*	*	0.29 (5)
F(1)				
x	0.3667 (6)	0.3758 (11)	0.362 (2)	0.3659 (3)
y	0.0540 (4)	0.0623 (13)	0.050 (2)†	0.0540 (2)
z	0.0824 (5)	0.0813 (9)	0.081 (2)	0.0824 (4)
$B[\text{\AA}^2]$	0.70 (5)	*	1.3 (4)	1.17 (3)
F(2)				
z	0.1855 (9)	0.1825 (17)	0.187 (2)	0.1871 (5)
$B[\text{\AA}^2]$	0.70 (5)	*	1.0 (4)	1.01 (6)
F(3)				
$B[\text{\AA}^2]$	0.70 (5)	*	1.7 (4)	1.60 (15)
R_{pr}	6.19%			12.53%
R_{wF}		18.5%	5.2%	

* Anisotropic temperature factors.

† Assumes a typographic error in the quoted y parameter.

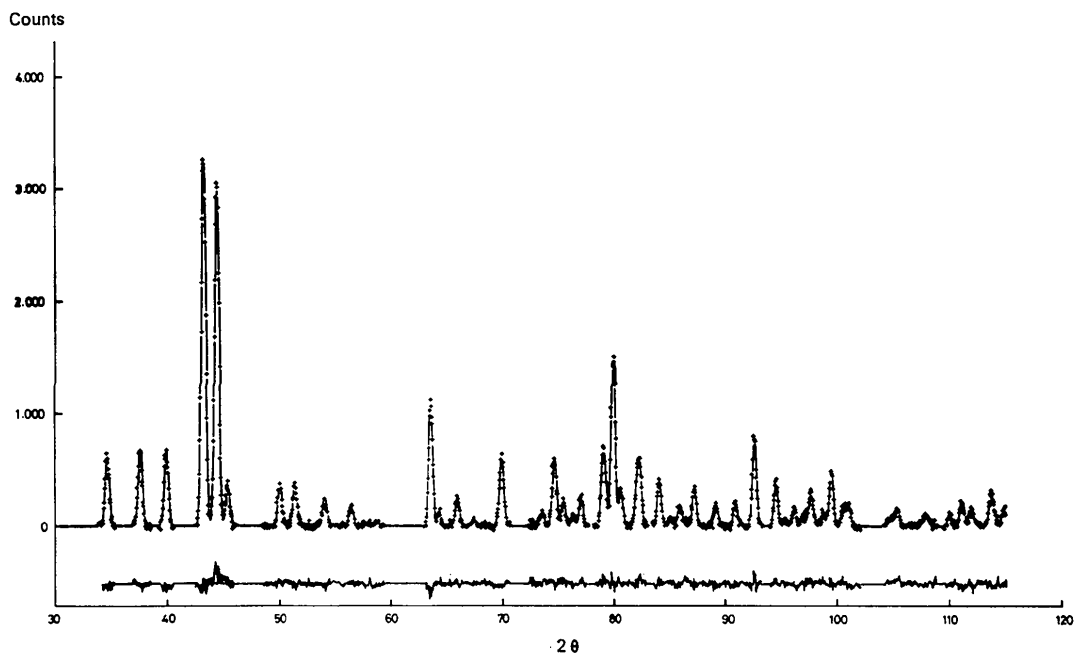


Fig. 2. Powder pattern of CeF₃ obtained on the high-resolution instrument D1A ($\lambda = 1.509 \text{ \AA}$): + observed intensity; - calculated intensity. Difference below.

resolution instrument D1A. Furthermore the profile for CeF_3 was calculated at intervals of 0.05° . In this case the isotropic temperature factors of the F atoms were individually refined. The arguments in favour of $P\bar{3}c1$ are the same as with LaF_3 . Final coordinates and temperature factors are given in Table 2 and the profile is shown in Fig. 2.

Table 3. *Interatomic distances for LaF_3 and CeF_3*

	LaF_3	CeF_3
Ln—2 F(2)	2.421 (5)	2.400 (3)
Ln—1 F(3)	2.436 (8)	2.419 (5)
Ln—2 F(1)	2.467 (4)	2.445 (3)
Ln—2 F(1)	2.482 (4)	2.460 (5)
Ln—2 F(1)	2.638 (8)	2.621 (5)
Ln—2 F(1)	2.999 (5)	2.974 (4)
F(1)—1 F(1)	2.575 (6)	2.532 (4)
F(1)—1 F(1)	2.688 (7)	2.677 (4)
F(1)—1 F(2)	2.694 (4)	2.668 (3)
F(1)—2 F(1)	2.746 (6)	2.719 (2)
F(1)—1 F(3)	2.755 (5)	2.728 (3)
F(1)—1 F(2)	2.776 (5)	2.761 (2)
F(1)—1 F(2)	2.868 (4)	2.855 (3)

Discussion

Taken with the indirect evidence our results confirm that the structures of LaF_3 and CeF_3 are correctly described by $P\bar{3}c1$ and the important interatomic distances are given in Table 3. The coordination sphere of La contains nine F atoms at distances between 2.421 and 2.638 Å, with two more distant neighbours at 2.999 Å. The coordination around Ce is the same except that the distances are shorter because of the

smaller ionic radius of Ce^{3+} . Distances for CeF_3 have been calculated with our cell constants, those for LaF_3 with the values of Zalkin & Templeton (1953).

The neutron results of LaF_3 and CeF_3 are strikingly similar (Table 2). Considering the very short counting time, the restricted number of data points and the low resolution in the LaF_3 experiment, the results compare very favourably with those on CeF_3 . It is clear that profile analysis of data collected on the low resolution instrument D2 affords a rapid and reliable method for refining simple crystal structures of this type. The higher resolution and thus the more reliable determination of the background gives however a higher precision for the temperature factor refinement.

References

- AFANASIEV, M. L., HABUDA, S. P. & LUNDIN, A. G. (1972). *Acta Cryst.* **B28**, 2903–2905.
 BAUMAN, R. P. & PORTO, S. P. S. (1967). *Phys. Rev.* **161**, 842–847.
 MANSMANN, M. (1965). *Z. Kristallogr.* **122**, 375–398.
 NEWMAN, D. J. & CURTIS, M. M. (1969). *J. Phys. Chem. Solids*, **30**, 2731–2737.
 OFTEDAL, I. (1931). *Z. Phys. Chem.* **13**, 190–200.
 RANGO, C. DE, TSOUCHARIS, G. & ZELWER, C. (1966). *C. R. Acad. Sci. Paris, Sér. C*, **263**, 64–66.
 RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
 SHULL, C. G. (1972). Massachusetts Institute of Technology Compilation.
 ZALKIN, A. & TEMPLETON, D. H. (1953). *J. Amer. Chem. Soc.* **75**, 2453.
 ZALKIN, A., TEMPLETON, D. H. & HOPKINS, T. E. (1966). *Inorg. Chem.* **5**, 1466–1468.

Acta Cryst. (1976). **B32**, 97

The Crystal and Molecular Structure of N,N' -Ethylenebis(thiosalicylideneiminato)cobalt(II), the Sulphur Analogue of a Molecular Oxygen Carrier, N,N' -Ethylenebis(salicylideneiminato)cobalt (II)

BY GARY D. FALLON AND BRYAN M. GATEHOUSE

Department of Chemistry, Monash University, Wellington Road, Clayton, Victoria, Australia, 3168

(Received 20 May 1975; accepted 23 May 1975)

The structure of N,N' -ethylenebis(thiosalicylideneiminato)cobalt(II) has been determined from 2727 diffractometer data and refined by least-squares methods to $R=0.041$. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a=13.978(6)$, $b=15.173(7)$, $c=7.103(4)$ Å, $\beta=98.14(8)^\circ$, $D_m=1.57$, $D_c=1.59$ g cm $^{-3}$ for $Z=4$. The molecules associate to form centrosymmetric dimers, similar to those in $\text{Co}(\text{salen})$. The coordination about Co is best described as square-pyramidal with the metal atom raised $0.181(1)$ Å out of the basal plane toward the apical S atom. The Co–S(apical) length is $2.444(1)$ Å.

Introduction

Synthetic molecular oxygen carriers are the object of much study (Basolo, 1974; Henrici-Olivé & Olivé,

1974). N,N' -Ethylenebis(salicylideneiminato)cobalt(II), $\text{Co}(\text{salen})$, the 'active form' of which absorbs molecular oxygen reversibly in the solid state as well as in solution has undergone extensive investigation (Bayer &