

METAL-ORGANIC COMPOUNDS

Acta Cryst. (1994). **C50**, 1537–1540

A Three-Dimensional Framework Aluminophosphate $(\text{CH}_3\text{NH}_3)^+[\text{Al}_3\text{P}_3\text{O}_{13}\text{H}]^-$

ANN M. CHIPPINDALE

*Chemical Crystallography Laboratory,
University of Oxford, 9 Parks Road,
Oxford OX1 3PD, England*

ANTHONY V. POWELL

*Department of Chemistry, Heriot-Watt University,
Edinburgh EH14 4AS, Scotland*

RICHARD H. JONES

*Department of Chemistry, University of Keele,
Staffordshire ST5 5BG, England*

JOHN M. THOMAS

*Davy Faraday Research Laboratory,
The Royal Institution, 21 Albemarle Street,
London W1X 4BS, England*

ANTHONY K. CHEETHAM

*Department of Materials, University of California,
Santa Barbara, CA 93106, USA*

QISHENG HUO AND RUREN XU

*Department of Chemistry, Jilin University, Changchun,
People's Republic of China*

(Received 28 October 1993; accepted 31 March 1994)

Abstract

The title compound, previously designated as JDF-2 [Gai-Boyes, Thomas, Wright, Jones, Natarajan, Chen & Xu (1992). *J. Phys. Chem.* **96**, 8206–8209], is an aluminium phosphate (AIPO) with a three-dimensional framework structure consisting of three types of PO_4 tetrahedral unit linked to three crystallographically distinct Al atoms. One of the Al atoms is tetrahedrally coordinated (as AlO_4) while the remaining two have distorted trigonal bipyramidal coordination and are linked through a common O atom to form $\text{O}_4\text{Al—OH—AlO}_4$ units. These units are relatively rare features in AIPO frameworks as the Al- and P-containing polyhedra are usually linked in a strictly alternating manner.

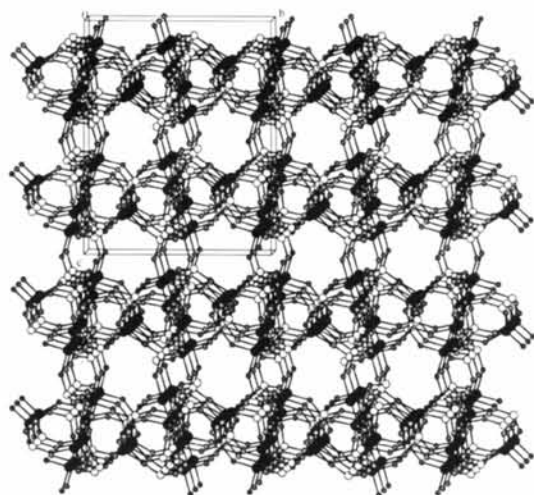
Comment

Since the synthesis of the first microporous aluminium phosphates (Wilson, Lok, Messing, Cannan & Flanigen, 1982), a number of other three-dimensional framework compounds have been characterized. The impetus for this research arises from the zeolitic nature of such materials, their possible sorption properties and use of their heteroatom-substituted derivatives in catalysis. Although in the majority of cases the Al and P atoms occupy sites with tetrahedral coordination, a few phases containing aluminium with a coordination number greater than four have been characterized; for example, AIPO-EN3 (Parise, 1985) and AIPO-21 (Bennett, Cohen, Artioli, Pluth & Smith, 1985), which have related structures, contain trigonal bipyramidal aluminium, and AIPO-15 (Pluth, Smith, Bennett & Cohen, 1984) contains octahedrally coordinated aluminium. All these compounds were prepared under aqueous conditions. Our work, however, has concentrated on the synthesis of AIPO's under non-aqueous conditions and this has led to the discovery of a number of new structures, both chain and layered as well as three-dimensional (Jones *et al.*, 1991; Chippindale *et al.*, 1992). Here we report the structure of a phase of JDF-2 closely related to that of AIPO-EN3, which was synthesized in ethylene glycol in the presence of methylamine. A high-resolution electron microscopy study of this compound has been reported previously (Gai-Boyes *et al.*, 1992).

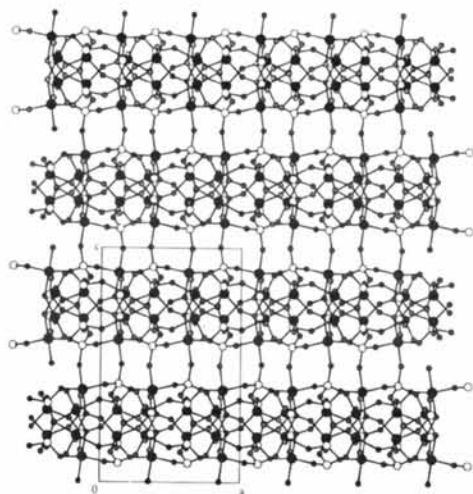
The structure of JDF-2 (Fig. 1) is a centrosymmetric variant of that of AIPO-EN3 [$a = 10.292$ (2), $b = 13.636$ (2), $c = 17.344$ (3) Å; space group $P2_12_12_1$] possessing the same framework topology and containing three-, four-, five- and eight-membered rings. In both cases, the template amine cation resides in the eight-membered-ring channels. The basic structural units, all of which have shared vertices, are P- and Al-centred tetrahedra and Al-centred trigonal bipyramids. The three types of PO_4 group and the Al(3)O_4 group have close to ideal tetrahedral geometry with P—O and Al—O distances in the ranges 1.506 (4)–1.543 (4) and 1.723 (4)–1.745 (4) Å, respectively, and O—P—O and O—Al—O angles in the ranges 106.1 (2)–112.8 (2) and 107.3 (2)–112.0 (2)°, respectively. These distances are close to those found in other tetrahedrally linked aluminium phosphates; *e.g.* in berlinite, the average P—O and Al—O distances are 1.516 and 1.739 Å, respectively (Schwarzenbach, 1966). The two remaining Al atoms, Al(1) and Al(2), have distorted trigonal bipyramidal coordination ($\text{O}_{\text{eq}}\text{—Al—O}_{\text{eq}}$ 106.3 (2)–135.5 (2), $\text{O}_{\text{eq}}\text{—Al—O}_{\text{ax}}$ 86.8 (2)–93.7 (2)°; average

Al—O_{eq} 1.790, average Al—O_{ax} 1.891 Å) and are linked through a shared O atom, O(3). This is situated in an axial position of the Al(2)O₅ trigonal bipyramid and in an equatorial position in Al(1)O₅ (Fig. 2), with Al(2)—O(3) and Al(1)—O(3) bond lengths of 1.902 (3) and 1.813 (3) Å, respectively. Bond–valence calculations (Brown & Altermatt, 1985) suggested that O(3) had unsatisfied valence; an H atom was subsequently located in a difference Fourier map at ~ 1 Å from O(3). Such Al₂O₉(OH) units with similar Al—OH bond lengths have been identified previously in AlPO-21 and AlPO-EN3. The O(3)H \cdots O(6) distance across the five-membered ring is sufficiently short (2.82 Å) for hydrogen bonding to take place. Hydrogen-bond interactions

between the methylamine cations and the aluminium phosphate framework appear to be weak (N \cdots O \geq 3.04 Å). However, attempts to detemplate the material (at ~ 623 K) led to the breakdown of the structure and the formation of an amorphous product.



(a)



(b)

Fig. 1. Two views (CAMERON; Pearce, Prout & Watkin, 1993) of the JDF-2 framework (a) along [100] and (b) along [010] with the methylamine template omitted for clarity.

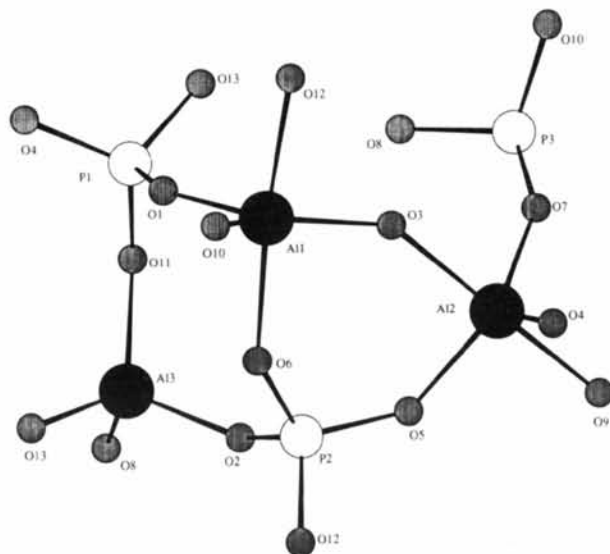


Fig. 2. Local view (CAMERON; Pearce, Prout & Watkin, 1993) of the coordination polyhedra showing the linkage of the Al(1) and Al(2) trigonal bipyramids. H(111) is omitted for clarity.

Experimental

The compound was synthesized *via* a gel precursor by adding phosphoric acid to a stirred suspension of aluminium isopropoxide in ethylene glycol (EG) and then adding methylamine to give a gel of composition Al₂O₃:P₂O₅:MeNH₂:EG 1:2.4:10:60. The gel was heated under autogeneous conditions in a sealed Teflon container at 453 K for 10 d. The resulting crystals were filtered and dried in air. X-ray microanalysis using a Jeol 2000FX electron microscope fitted with a Tracor Northern analysis system confirmed that the product was monophasic with a P:Al ratio of approximately 1:1. CHN analysis gave the following results: N 3.41, C 2.95, H 1.60%.

Crystal data

$(\text{CH}_3\text{NH}_3)[\text{Al}_3\text{P}_3\text{O}_{13}\text{H}]$

$M_r = 414.93$

Orthorhombic

$Pcab$

$a = 10.281(2)$ Å

$b = 13.844(3)$ Å

$c = 17.064(5)$ Å

$V = 2428.72$ Å³

$Z = 8$

$D_x = 2.270$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 20 reflections

$\theta = 15.1\text{--}16.5^\circ$

$\mu = 0.76$ mm⁻¹

$T = 293$ K

Plate

$0.23 \times 0.09 \times 0.05$ mm

Transparent

Data collection

Enraf–Nonius CAD-4 diffractometer

$R_{\text{int}} = 0.0279$

$\theta_{\text{max}} = 23^\circ$

$\omega/2\theta$ scans	$h = -1 \rightarrow 11$
Absorption correction:	$k = -1 \rightarrow 15$
empirical	$l = -1 \rightarrow 18$
$T_{\min} = 0.89$, $T_{\max} = 1.00$	3 standard reflections
2803 measured reflections	frequency: 60 min
1683 independent reflections	intensity variation: none
1343 observed reflections	
$[I > 1.5\sigma(I)]$	
Refinement	
Refinement on F	$(\Delta/\sigma)_{\max} = 0.004$
$R = 0.0476$	$\Delta\rho_{\max} = 0.55 \text{ e } \text{\AA}^{-3}$
$wR = 0.0456$	$\Delta\rho_{\min} = -0.48 \text{ e } \text{\AA}^{-3}$
$S = 1.38$	Extinction correction: none
1343 reflections	Atomic scattering factors
190 parameters	from <i>International Tables</i>
Weighting scheme:	for <i>X-ray Crystallography</i>
Chebyshev, three-term	(1974, Vol. IV)
polynomial	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
P(1)	0.3676 (1)	0.25328 (9)	0.20387 (7)	0.0108
P(2)	0.1263 (1)	0.46013 (9)	0.33711 (7)	0.0109
P(3)	0.6293 (1)	0.43332 (8)	0.41973 (7)	0.0093
Al(1)	0.3298 (1)	0.4789 (1)	0.19812 (8)	0.0108
Al(2)	0.3749 (1)	0.5617 (1)	0.39344 (8)	0.0102
Al(3)	0.1219 (1)	0.2414 (1)	0.30632 (8)	0.0126
O(1)	0.3270 (3)	0.3531 (2)	0.1774 (2)	0.0179
O(2)	0.1182 (4)	0.3512 (2)	0.3555 (2)	0.0261
O(3)	0.4036 (3)	0.5182 (2)	0.2892 (2)	0.0144
O(4)	0.3587 (3)	0.6857 (2)	0.3650 (2)	0.0174
O(5)	0.2204 (3)	0.5024 (3)	0.3959 (2)	0.0160
O(6)	0.1685 (3)	0.4763 (2)	0.2530 (2)	0.0137
O(7)	0.5333 (3)	0.5167 (2)	0.4155 (2)	0.0147
O(8)	0.0771 (3)	0.1529 (2)	0.3726 (2)	0.0169
O(9)	0.3502 (3)	0.5991 (2)	0.4967 (2)	0.0141
O(10)	0.2606 (3)	0.5375 (2)	0.1149 (2)	0.0142
O(11)	0.2779 (3)	0.2193 (3)	0.2703 (2)	0.0218
O(12)	-0.0054 (3)	0.5047 (3)	0.3513 (2)	0.0167
O(13)	0.0076 (3)	0.2450 (3)	0.2325 (2)	0.0194
N(1)	0.4452 (7)	0.6379 (6)	-0.0060 (4)	0.0641
C(1)	0.396 (1)	0.7386 (7)	-0.0152 (6)	0.0725

Table 2. Selected geometric parameters (\AA , $^\circ$)

P(1)—O(1)	1.513 (3)	Al(1)—O(6)	1.905 (3)
P(1)—O(4)	1.506 (4)	Al(1)—O(10)	1.783 (3)
P(1)—O(11)	1.535 (4)	Al(1)—O(12)	1.906 (3)
P(1)—O(13)	1.521 (3)	Al(2)—O(3)	1.902 (3)
P(2)—O(2)	1.543 (4)	Al(2)—O(4)	1.791 (3)
P(2)—O(5)	1.511 (4)	Al(2)—O(5)	1.789 (3)
P(2)—O(6)	1.515 (4)	Al(2)—O(7)	1.784 (3)
P(2)—O(12)	1.508 (3)	Al(2)—O(9)	1.853 (3)
P(3)—O(7)	1.520 (3)	Al(3)—O(2)	1.737 (4)
P(3)—O(8)	1.536 (4)	Al(3)—O(8)	1.730 (3)
P(3)—O(9)	1.510 (3)	Al(3)—O(11)	1.745 (4)
P(3)—O(10)	1.528 (3)	Al(3)—O(13)	1.723 (4)
Al(1)—O(1)	1.777 (3)	N(1)—C(1)	1.49 (1)
Al(1)—O(3)	1.813 (3)		
O(1)—P(1)—O(4)	108.6 (2)	O(3)—Al(2)—O(5)	90.8 (2)
O(1)—P(1)—O(11)	109.5 (2)	O(4)—Al(2)—O(5)	111.3 (2)
O(4)—P(1)—O(11)	110.5 (2)	O(3)—Al(2)—O(7)	86.8 (2)
O(1)—P(1)—O(13)	110.1 (2)	O(4)—Al(2)—O(7)	118.5 (2)
O(4)—P(1)—O(13)	108.5 (2)	O(5)—Al(2)—O(7)	130.2 (2)
O(11)—P(1)—O(13)	109.6 (2)	O(3)—Al(2)—O(9)	177.4 (2)
O(2)—P(2)—O(5)	106.1 (2)	O(4)—Al(2)—O(9)	88.7 (2)
O(2)—P(2)—O(6)	112.8 (2)	O(5)—Al(2)—O(9)	89.1 (2)
O(2)—P(2)—O(12)	108.6 (2)	O(7)—Al(2)—O(9)	91.3 (2)
O(5)—P(2)—O(12)	108.1 (2)	O(2)—Al(3)—O(8)	107.3 (2)
O(6)—P(2)—O(12)	110.4 (2)	O(2)—Al(3)—O(11)	110.1 (2)
O(7)—P(3)—O(8)	109.7 (2)	O(8)—Al(3)—O(11)	110.5 (2)
O(7)—P(3)—O(9)	111.2 (2)	O(2)—Al(3)—O(13)	108.3 (2)
O(8)—P(3)—O(9)	108.2 (2)	O(8)—Al(3)—O(13)	108.5 (2)
O(7)—P(3)—O(10)	110.8 (2)	O(11)—Al(3)—O(13)	112.0 (2)
O(8)—P(3)—O(10)	108.1 (2)	P(1)—O(1)—Al(1)	146.3 (2)
O(9)—P(3)—O(10)	108.7 (2)	P(2)—O(2)—Al(3)	139.1 (3)
O(1)—Al(1)—O(3)	118.1 (2)	Al(1)—O(3)—Al(2)	146.3 (2)
O(1)—Al(1)—O(6)	93.7 (2)	P(1)—O(4)—Al(2)	143.2 (2)
O(3)—Al(1)—O(6)	87.1 (2)	P(2)—O(5)—Al(2)	136.9 (2)
O(1)—Al(1)—O(10)	106.3 (2)	P(2)—O(6)—Al(1)	135.9 (2)
O(3)—Al(1)—O(10)	135.5 (2)	P(3)—O(7)—Al(2)	150.3 (2)
O(6)—Al(1)—O(10)	93.0 (2)	P(3)—O(8)—Al(3)	143.1 (2)
O(1)—Al(1)—O(12)	92.5 (2)	P(3)—O(9)—Al(2)	142.8 (2)
O(3)—Al(1)—O(12)	88.3 (2)	P(3)—O(10)—Al(1)	141.3 (2)
O(6)—Al(1)—O(12)	173.5 (2)	P(1)—O(11)—Al(3)	139.4 (2)
O(10)—Al(1)—O(12)	87.0 (2)	P(2)—O(12)—Al(1)	140.9 (2)
O(3)—Al(2)—O(4)	93.7 (2)	P(1)—O(13)—Al(3)	151.7 (2)

A suitable crystal was mounted on a glass fibre using 'superglue' (cyanoacrylate). The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985) and refined by full-matrix least squares using the *CRYSTALS* suite of programs (Watkin, Carruthers & Betteridge, 1985). H atoms on the organic fragment were located initially in the difference Fourier maps, but subsequently placed geometrically and allowed to ride on the atoms to which they were attached with isotropic temperature factors fixed at 0.01 \AA^2 .

One of us (AMC) thanks the University of Oxford for a Glasstone Research Fellowship and the Royal Society for a Research Grant.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DU1073). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Bennett, J. M., Cohen, J. M., Artioli, G., Pluth, J. J. & Smith, J. V. (1985). *Inorg. Chem.* **24**, 188–193.
- Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* **B41**, 244–247.
- Chippindale, A. M., Powell, A. V., Bull, L. M., Jones, R. H., Cheetham, A. K., Thomas, J. M. & Xu, R. (1992). *J. Solid State Chem.* **96**, 199–210.
- Gai-Boyes, P. I., Thomas, J. M., Wright, P. A., Jones, R. H., Natarajan, S., Chen, J. & Xu, R. (1992). *J. Phys. Chem.* **96**, 8206–8209.
- Jones, R. H., Thomas, J. M., Xu, R., Huo, Q., Cheetham, A. K. & Powell, A. V. (1991). *J. Chem. Soc. Chem. Commun.* pp. 1266–1268.
- Parise, J. M. (1985). *Zeolites*, edited by B. Drzaj, S. Hocevar & S. Pejovnik, pp. 271–278. Amsterdam: Elsevier.
- Pearce, L. J., Prout, C. K. & Watkin, D. J. (1993). *CAMERON User Guide*, Chemical Crystallography Laboratory, Univ. of Oxford, England.
- Pluth, J. J., Smith, J. V., Bennett, J. M. & Cohen, J. P. (1984). *Acta Cryst.* **C40**, 2008–2011.
- Schwarzenbach, D. (1966). *Z. Kristallogr.* **12**, 161.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

- Watkin, D. J., Carruthers, J. R. & Betteridge, P. W. (1985). *CRYSTALS User Guide*. Chemical Crystallography Laboratory, Univ. of Oxford, England.
- Wilson, S. T., Lok, B. M., Messing, C. A., Cannan, T. R. & Flanigen, E. M. (1982). *J. Am. Chem. Soc.* **104**, 1146–1147.

Acta Cryst. (1994). **C50**, 1540–1541

Di- μ -fluoro-bis[bis(*N,N*-dimethylformamide)trifluorozirconium(IV)]

WILLIAM ERRINGTON AND MATTHEW A. ISMAIL

Department of Chemistry, University of Warwick,
Coventry CV4 7AL, England

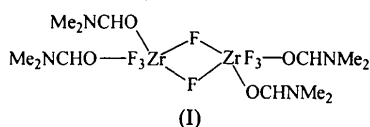
(Received 17 March 1994; accepted 26 May 1994)

Abstract

The title compound, $[\text{ZrF}_3(\text{C}_3\text{H}_7\text{NO})_2(\mu\text{-F})_2]$, is a centrosymmetric fluorine-bridged dimer. The seven-coordinate Zr atoms are in a pentagonal bipyramidal environment with F atoms above and below the pentagonal plane. The average Zr—F bridging distance of 2.147 (4) Å is significantly longer than the mean terminal distance of 1.962 (4) Å.

Comment

The structure of the title compound (I) has been determined as part of a continuing study of ZrF_4 adducts (Alcock, Errington, Golby, Patterson & Wallbridge, 1994). The compound obtained by refluxing ZrF_4 with *N,N*-dimethylformamide (dmf) has been reported (Muettterties, 1960) as a 1:1 adduct, but the material investigated in this work is clearly the 1:2 adduct (I).



The molecular structure is shown in Fig. 1. It consists of two pentagonal bipyramidal units linked *via* two F-atom bridges to give a centrosymmetric dimer. The equatorial ligand donor atoms are almost coplanar: F3 and O21 are 0.038 (5) and 0.056 (3) Å, respectively, above the plane of Zr1, F4, Zr1ⁱ and F4ⁱ, while O11 is 0.073 (5) Å below the plane. The axial F atoms, F1 and F2, are displaced 1.952 (4) Å from this plane. The mean length of the terminal Zr—F bonds is 1.962 (4) Å, while, as expected, the bridging Zr—F bonds are longer, averaging 2.147 (4) Å.

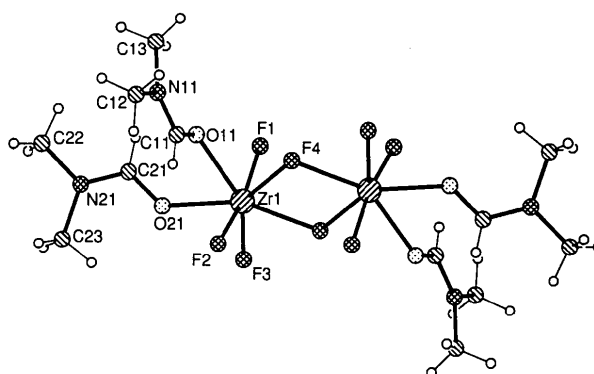


Fig. 1. View of the molecule showing the non-H-atom labelling.

Relatively few structures have been reported involving coordinated dmf, but in all cases it bonds through the O atom (Goggin, 1987). In the title compound, the Zr1—O21 and Zr1—O11 distances [2.227 (3) and 2.239 (4) Å, respectively] are similar to those reported for the Zr—O bond lengths [2.253 (2) and 2.198 (2) Å] in $\text{CpZrCl}_3(\text{dmf})_2$ (Erker *et al.*, 1990). Furthermore, the ligand bond lengths C11—N11 and C21—N21 of 1.298 (6) and 1.304 (5) Å, respectively, are indicative of some double-bond character, and agree with earlier results (Holt, Alcock, Sumner & Asplund, 1979; Erker *et al.*, 1990). Two dmf ligands are located almost along the Zr1···Zr1ⁱ axis [Zr1ⁱ···Zr—O21 = 176.51 (8)°], with the other pair at an angle of 103.65 (12)° to this axis. The coordination sites for the dmf ligands contrast with those reported previously (Alcock, Errington, Golby, Patterson & Wallbridge, 1994) for the analogous dimethyl sulfoxide complex $[\text{ZrF}_4(\text{Me}_2\text{SO})_2]_2$, where the Zr···Zr—O angles are all about 103°.

Experimental

The complex was prepared by refluxing ZrF_4 in *N,N*-dimethylformamide (Muettterties, 1960) and allowed to crystallize upon cooling. The complex decomposes slowly in air and was, therefore, covered in a layer of Nujol prior to fixing onto a quartz fibre. Decomposition was further reduced by collecting the data with the crystal at 230 K under a stream of dry air.

Crystal data

$[\text{ZrF}_4(\text{C}_3\text{H}_7\text{NO})_2]$

$M_r = 313.41$

Triclinic

$P\bar{1}$

$a = 8.369$ (8) Å

$b = 8.899$ (7) Å

$c = 9.501$ (12) Å

$\alpha = 96.40$ (8)°

$\beta = 114.53$ (9)°

$\gamma = 115.50$ (6)°

$V = 543.5$ (10) Å³

$Z = 2$

$D_x = 1.915$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 18 reflections

$\theta = 8$ –9°

$\mu = 1.052$ mm⁻¹

$T = 230$ (2) K

Flat block

$0.36 \times 0.09 \times 0.06$ mm

Colourless