$(HPO_3H)_2.H_2O$ (Larbot *et al.*, 1984) ou complexes tels que $HP_2O_6H_2^{2-}$ dans $Cd(HPO_3H)_2.H_2O$ (Loub *et al.*, 1978) ou $H_3P_3O_9H_3^{3-}$ dans $La(HPO_3H)_3.H_2O$. Par contre dans le cas des phosphites neutres seul le groupement PO_3H^{2-} isolé a pu être mis en évidence comme dans $(NH_4)_2PO_3H.H_2O$ (Rafiq, Durand & Cot, 1982).

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Diammonium Hexafluorozirconate

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Abstract. $(NH_4)_2ZrF_6$, $M_r = 241{\cdot}29$, orthorhombic, $Pca2_1$, $a = 13{\cdot}398\,(8)$, $b = 7{\cdot}739\,(3)$, $c = 11{\cdot}680\,(4)$ Å, $V = 1211{\cdot}1$ Å^3, $Z = 8$, $D_x = 2{\cdot}65$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 18{\cdot}36$ cm^{-1}, $F(000) = 928$, $T = 296$ K, $R = 0{\cdot}026$ for 6359 $[F^2 > \sigma(F^2)]$ of 7225 total unique data. Zr_2F_{12} units extend in an infinite chain along the c axis. Each Zr has 8 fluorine neighbors with distances ranging from 2·02 to 2·34 Å.

Experimental. Diammonium hexafluorozirconate was investigated for its second-harmonic generating properties, and a crystal structure was determined to study the relationship of the structure to the optical properties. Crystals of the title compound were purchased from Cleveland Crystals Inc. Colorless crystal, 0·16 × 0·19 × 0·34 mm; modified Picker automatic diffractometer, graphite monochromator; cell dimensions from 35 reflections, $20 < 2\theta < 33°$; analytical absorption correction, range 1·29 to 1·44; max. $(\sin\theta)/\lambda = 1{\cdot}00$ Å^{-1}, h 0 to 26, k 0 to 15, l −23 to 16; four standard reflections, $\sigma = 2{\cdot}3, 3{\cdot}1, 1{\cdot}7, 3{\cdot}8\%$, data corrected for variations; 7237 data, 7225 unique (Friedel pairs not combined), $R_{\text{int}} = 0{\cdot}026$, 33 data $[(\sin\theta)/\lambda < 0{\cdot}15$ Å$^{-1}]$ given zero weight; Zr positions from Patterson function, remaining atomic positions from ΔF maps; refinement on F, 6359 $F > \sigma(F^2)$ data, non-hydrogen atoms anisotropic, H atoms included with distance constraints (Waser, 1963), tetrahedral geometry, and isotropic thermal parameters (thermal parameters of H atoms of the same ammonium group constrained to the same value); 215 parameters [one scale factor, 18 anisotropic atoms (z parameter of Zr is fixed), 16 H atoms with four isotropic thermal parameters, and a Rogers (1981) parameter η]; $R = 0{\cdot}026$ (non-zero weighted data); R (all data) $= 0{\cdot}035$; $wR = 0{\cdot}034$; $S = 1{\cdot}10$; $w = 4F^2/[\sigma^2(F^2) + (0{\cdot}04F^2)^2]$; $\eta = 1{\cdot}22\,(6)$; max. $\Delta/\sigma < 0{\cdot}002$; max. empirical isotropic correction for extinction 30% of F; max. and min. of ΔF synthesis 0·8 and −0·6 e Å^{-3}; scattering factors from *International Tables for X-ray Crystallography* (1974); local unpublished programs and *ORTEP* (Johnson, 1965). Atomic coordinates are listed in Table 1,* with the atomic numbering scheme shown in Fig. 1. Selected distances and angles are given in Table 2.

Discussion. The structure consists of Zr_2F_{12} units extended in infinite chains along the c axis and ammonium ions hydrogen bonded in a complex three-dimensional network to these chains. The Zr atoms are each coordinated to eight F atoms. A triangle

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, distance restraints, interatomic distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51198 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional and thermal parameters with e.s.d.'s in parentheses*

$B_{eq} = \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j / 3.$

	x	y	z	B_{eq}(Å^2)
Zr1	0·14048 (1)	0·48282 (2)	0	1·045 (2)
Zr2	0·11117 (1)	0·03603 (2)	−0·00787 (2)	1·128 (3)
F1	0·12476 (9)	0·75924 (12)	−0·00672 (26)	2·51 (3)
F2	0·00168 (12)	0·52923 (18)	0·06115 (18)	2·72 (4)
F3	0·19582 (14)	0·55080 (21)	0·15627 (13)	2·69 (3)
F4	0·10700 (13)	0·53078 (19)	−0·16742 (14)	2·25 (3)
F5	0·28276 (10)	0·56086 (18)	−0·04137 (14)	2·35 (3)
F6	0·03549 (11)	0·26096 (16)	−0·06392 (17)	2·61 (3)
F7	0·12713 (12)	0·25859 (16)	0·11193 (15)	3·03 (4)
F8	0·21537 (10)	0·25943 (16)	−0·06401 (18)	2·83 (3)
F9	−0·02564 (12)	−0·04447 (20)	−0·06919 (19)	3·38 (4)
F10	0·03649 (13)	−0·02269 (21)	0·13938 (15)	2·67 (3)
F11	0·15745 (17)	−0·01582 (21)	−0·16972 (14)	2·78 (4)
F12	0·24375 (13)	−0·01349 (21)	0·06727 (20)	3·17 (4)
N1	0·11670 (14)	0·75120 (24)	−0·35768 (21)	2·03 (4)
N2	0·09058 (15)	0·3432 (3)	0·33845 (17)	2·06 (4)
N3	0·15629 (17)	0·8265 (3)	0·31164 (20)	2·67 (5)
N4	0·13318 (16)	0·24838 (26)	−0·33461 (25)	2·56 (5)

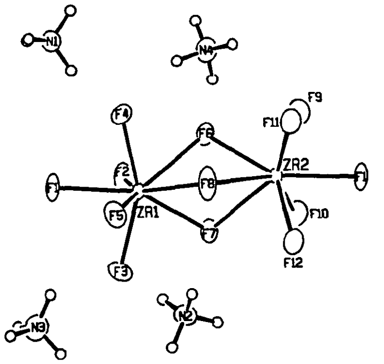

Fig. 1. *ORTEP* drawing (Johnson, 1965) showing the atomic numbering scheme. 50% probability ellipsoids are shown.

of three F atoms, at the center of the Zr_2F_{12} group, is sandwiched between two Zr atoms. Square pyramids of five F atoms are coordinated to the other side of the Zr atoms; the apex F atom of this pyramid is shared by the adjacent Zr_2F_{12} groups. The shared Zr—F distances range from 2·12 to 2·34 Å and the non-sharing Zr—F distances range from 2·02 to 2·06 Å.

The optical properties of the title compound are reported elsewhere (Velsko, 1986).

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Table 2. *Selected distances* (Å) *and angles* (°) *in* $(NH_4)_2ZrF_6$

F1—Zr1	2·1510 (12)	F6—N1	3·157 (3)
F2—Zr1	2·0242 (18)	F10—N1	2·9374 (27)
F3—Zr1	2·0391 (16)	F11—N1	2·8929 (29)
F4—Zr1	2·0403 (17)	F12—N1	2·7533 (25)
F5—Zr1	2·0572 (17)	F2—N2	3·045 (3)
F6—Zr1	2·3418 (15)	F3—N2	3·0163 (27)
F7—Zr1	2·1800 (16)	F4—N2	2·822 (3)
F8—Zr1	2·1341 (14)	F5—N2	2·7729 (25)
Zr2—Zr1	3·4812 (13)	F7—N2	2·7691 (27)
F1—Zr2	2·1499 (13)	F8—N2	2·9116 (28)
F6—Zr2	2·1183 (14)	F9—N2	2·6953 (28)
F7—Zr2	2·2294 (16)	F3—N3	2·8508 (30)
F8—Zr2	2·3170 (15)	F5—N3	2·8002 (29)
F9—Zr2	2·0641 (18)	F6—N3	3·0287 (30)
F10—Zr2	2·0410 (17)	F9—N3	2·8012 (29)
F11—Zr2	2·0295 (17)	F10—N3	2·8260 (30)
F12—Zr2	2·0180 (18)	F11—N3	2·786 (3)
F2—N1	2·8502 (25)	F2—N4	2·7765 (27)
F3—N1	2·9566 (29)	F4—N4	2·9517 (30)
F4—N1	2·8045 (28)	F10—N4	2·883 (3)
F5—N1	2·9304 (28)	F11—N4	2·828 (3)
		F12—N4	2·8530 (28)
F1—Zr1—F2	75·31 (6)	F1—Zr2—F8	133·97 (6)
F1—Zr1—F3	79·14 (9)	F1—Zr2—F9	77·10 (6)
F1—Zr1—F4	76·26 (9)	F1—Zr2—F10	79·30 (9)
F1—Zr1—F5	77·89 (6)	F1—Zr2—F11	77·46 (9)
F1—Zr1—F6	131·20 (6)	F1—Zr2—F12	74·54 (6)
F1—Zr1—F7	143·66 (9)	F6—Zr2—F7	66·73 (6)
F1—Zr1—F8	147·02 (7)	F6—Zr2—F8	65·65 (7)
F2—Zr1—F3	88·42 (8)	F6—Zr2—F9	73·48 (6)
F2—Zr1—F4	95·97 (8)	F6—Zr2—F10	102·05 (7)
F2—Zr1—F5	151·89 (6)	F6—Zr2—F11	91·20 (8)
F2—Zr1—F6	71·98 (7)	F6—Zr2—F12	135·38 (6)
F2—Zr1—F7	81·62 (6)	F7—Zr2—F8	62·83 (6)
F2—Zr1—F8	134·37 (5)	F7—Zr2—F9	122·42 (7)
F3—Zr1—F4	152·98 (6)	F7—Zr2—F10	71·95 (7)
F3—Zr1—F5	78·32 (7)	F7—Zr2—F11	135·08 (7)
F3—Zr1—F6	133·86 (6)	F7—Zr2—F12	77·84 (7)
F3—Zr1—F7	72·45 (6)	F8—Zr2—F9	131·46 (7)
F3—Zr1—F8	110·58 (8)	F8—Zr2—F10	134·42 (7)
F4—Zr1—F5	85·71 (7)	F8—Zr2—F11	72·54 (7)
F4—Zr1—F6	72·29 (7)	F8—Zr2—F12	74·60 (8)
F4—Zr1—F7	134·55 (6)	F9—Zr2—F10	77·87 (9)
F4—Zr1—F8	85·12 (7)	F9—Zr2—F11	83·60 (9)
F5—Zr1—F6	134·19 (6)	F9—Zr2—F12	151·07 (7)
F5—Zr1—F7	116·78 (6)	F10—Zr2—F11	152·96 (7)
F5—Zr1—F8	73·73 (6)	F10—Zr2—F12	91·30 (9)
F6—Zr1—F7	63·79 (6)	F11—Zr2—F12	95·66 (10)
F6—Zr1—F8	64·97 (7)	Zr1—F1—Zr2	178·11 (15)
F7—Zr1—F8	66·66 (7)	Zr1—F6—Zr2	102·50 (6)
F1—Zr2—F6	149·46 (7)	Zr1—F7—Zr2	104·27 (8)
F1—Zr2—F7	139·26 (9)	Zr1—F8—Zr2	102·83 (6)

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