The dta diagram of the amorphous form of Pb[OP(C6- H5)20]2 obtained as a residue from solution contains an irreversible exotherm at approximately 145 "C in addition to the melting endotherm above 225 \degree C. Examination of this material with a light-polarizing microscope equipped with a hot stage shows crystallization occurring at the temperature of the exotherm. The dta diagrams of the crystalline polymers contain only one transition, which is the endotherm due to melting.

The thermal decomposition of $Pb[OP(C₆H₅)₂O]$ ₂ was followed by tga in both air and nitrogen with a heating rate of 5 \degree C/min. Under these conditions the decompositions in both atmospheres were identical, with initial weight loss occurring at 300 "C. This is well below the initial weight loss observed for other diphenylphosphinates such as Zn[O- $P(C_6H_5)_2O_2^{15}$ and $Cr[OP(C_6H_5)_2O_2OH^{16}$

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Registry **No.** Pb[OP(C6Hs)z0]2, 58188-33-3.

Supplementary Material Available: Listing of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Geosciences, University of Marburg, D 355 Marburg, West Germany, and Department of Physical Chemistry I, Technische Hochschule, D61 Darmstadt, West Germany

Crystal Structure of an Adduct of Telluric Acid with Potassium Fluoride, Te(OH)6*2KF. A Compound with Short 0-H-F Hydrogen Bonds

R. ALLMANN^{*} and W. HAASE

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Te(OH)6.2KF crystallizes in space group *Pcab* with $Z = 4$ formula units per cell: $a = 9.610$ (4) Å, $b = 8.999$ (6) Å, c $= 8.547$ (5) Å, $V = 739.1$ Å³, $d_m = 3.08$ (3) g cm⁻³, $d_x = 3.11$ g cm⁻³. With 576 independent reflections (74 of them $\langle F_{\text{min}} = \sigma(F)$, which were measured on a Philips four-circle PW 1100 diffractometer, the structure could be refined to $R = 3.1\%$, using anisotropic temperature factors for all atoms except H. The structure is very similar to the cubic one of K₂PtCl₆, but to make room for the F- ions, the Te(OH)6 octahedra are slightly turned out of their regular positions (Te-0 = 1.905 **A).** K is ten-coordinated (K-0 = 2.766-3.225 **A,** eight times; K-F = 2.591, 3.125 **A).** All OH groups are involved in short 0-H-F hydrogen bonds of about 2.58 **A.** The fluorine ions are therefore four-coordinated (plus one long K-F bond). The ir and Raman spectra are discussed.

Introduction

Telluric acid, Te(OH)6, forms with alkali fluorides adducts like $Te(OH)_{6}$ -2KF or $Te(OH)_{6}$ -NaF.¹ In the case of the sodium compound rather regular Te(OH)6 octahedra were found² (Te-O = 1.92 Å). A bonding of the $F⁻$ ions directly to Te, as assumed by Kolditz and Fitz, $\frac{1}{2}$ could not be confirmed by this, but three of the six OH groups form strong O-H-F hydrogen bonds of 2.50 **A** in Te(OH)6*NaF2 (the other three O-H-0 bonds are 2.76 **A).** How the double amount of alkali and fluorine ions is assembled in the structure of $Te(OH)_{6}$ -2KF shall be examined in this paper, as well as the kind of hydrogen bonds in this compound. **A** preliminary structure determination by Willinger³ yielded wrong results with respect to the fluorine positions.

Experimental Section

A colorless octahedral crystal (form $\{111\}$) of Te(OH)6.2KF with about 0.2-mm edges was measured on a Philips four-circle PW 1100 diffractometer (Mo *Ka* radiation, *h* 0.71069 **A,** graphite monochromator, $\omega/2\theta$ scan, $\theta_{\text{max}} = 24^{\circ}$, scan width 1.2^o in θ , time for integrated reflection 40 s, time for background 2×10 s, scintillation counter with discriminator). For the stronger *eee* and ooo reflections mostly four symmetry-equivalent reflections were measured; for the

* To whom correspondence should be addressed at the University of Marburg.

others, mostly two (altogether 1821 reflections). After applying the normal *Lp* corrections and averaging, 576 independent structure factors remained, 74 of them below the observation limit $F_{\text{min}} = \sigma(F_0)$. No absorption correction was applied $(\mu = 53.0 \text{ cm}^{-1})$.

The centrosymmetric space group *Pcab* is uniquely determined by the following extinctions: $0k$ with $l = 2n$, $h0l$ with $h = 2n$, and $hk0$ with $k = 2n$ only. The lattice constants $a = 9.610$ (4) $\text{\AA}, b = 8.999$ (6) **A,** *c* = 8.547 (5) **A,** and *V* = 739.1 A3 were derived at room temperature (\sim 21 °C) from the 2 θ values of 14 selected reflections (200, 020, 002, 111, and symmetry-related ones), which were measured six times during 3 days at the four-circle goniometer. The given values and standard deviations result when these six data sets are taken with equal weight. The equivalent positions in *Pcab* are $\pm (x, y, z; \frac{1}{2} +$ $x, -y, \frac{1}{2} - z; \frac{1}{2} - x, \frac{1}{2} + y, -z; -x, \frac{1}{2} - y, \frac{1}{2} + z)$. With *Z* $=$ 4 formula units of Te(OH) $_6$ -2KF per unit cell the calculated density becomes $d_x = 3.11$ g cm⁻³, which compares well with the measured density $d_m = 3.08$ (3) g cm⁻³ (pycnometric with 189 mg of substance in 2 ml of n -hexane).

Structure Determination and Refinement

Since the tellurium atoms have to be situated at centers of symmetry, they contribute only to the *eee* and *ooo* reflections. Because of the high number of 52 electrons for Te, all *F* values of these 179 reflections are expected to become positive if Te is placed at position 4(a): 0, 0, 0; *112, '12,* 0; **112,** 0, *112;* 0, **1/2, '/2. A** Fourier synthesis with only these structure factors (i.e., in space group *Fmmm*, all signs

Atom	x	ν	z	$\overline{\sigma}(x, y, z)$	B_{11}	B_{22}	$\cdot B_{33}$	B_{12}	B_{13}	B_{23}	$\overline{\sigma}(B)$, A ²
Te					0.57	1.44	1.16	0.07	0.07	0.10	0.02
K	0.2257(1)	0.2460(2)	0.2224(1)	1.3	1.30	2.11	1.41	-0.30	-0.24	-0.13	0.05
F	0.3766(3)	0.3991(4)	0.4151(4)	3	0.98	2.51	2.09	0.02	0.03	-0.18	0.13
O(1)	0.1876(4)	0.0500(5)	$-0.0481(5)$	4	0.68	2.13	1.82	0.21	0.13	0.71	0.16
O(2)	$-0.0480(4)$	0.2044(5)	0.0275(5)	4	1.19	1.46	2.34	0.11	0.63	0.27	0.16
O(3)	0.0485(4)	$-0.0172(5)$	0.2150(5)	4	1.16	3.51	1.10	0.75	0.23	-0.14	0.17
H(1)	0.248(10)	$-0.001(7)$	$-0.011(8)$	76	$(1.5)^{o}$						
H(2)	$-0.011(7)$	0.247(9)	$-0.017(7)$	69	$(0.5)^{o}$						
H(3)	$-0.006(6)$	0.006(7)	0.274(9)	65	$(0.5)^{b}$						

 a $\sigma(x, y, z)$ is the averaged absolute standard deviation of the coordinates in 10⁻³ A. The temperature factor is defined as $\exp(-\frac{1}{4}\Sigma_{i=1}^{3}\Sigma_{j=1}^{3}B_{ij}h_{i}h_{i}a_{i}*\alpha_{i}^{*})$. B, A².

as +) revealed that the oxygen atoms are nearly, but not exactly, situated at the coordinate axes at about 0.2, 0, 0; 0, 0.2, 0; and 0, 0,0.2, and the potassium ions, near **1/4, 1/4,** 1/4. Furthermore a weak peak was found at about 0.4, 0.4, 0.4 representing $1/4$ F-, the other F ⁻ peaks being at about 0.1, 0.1, 0.4 and cyclical permutations. By fixing one full fluorine ion at 0.4,0.4,0.4, one out of the four possible fluorine positions, which are equivalent in *Fmmm,* was selected, and by doing so the space group symmetry was reduced to *Pcab.* With these starting parameters the structure could be refined with anisotropic temperature factors to $R = 3.5\%$ using all reflections (without H atoms).

Because the tellurium atoms contribute only to one-fourth of all reflections, the other atoms could be determined with rather high accuracy (see Table I) and in a Δ Fourier synthesis all three independent hydrogen atoms could be clearly seen (peak heights 0.6-0.8 $e/A³$. No other interesting features could be detected in this Fourier map (highest spurious peak $0.3 \frac{e}{\text{A}}^3$ near the Te position).

After taking the H atoms into account (fixed isotropic temperature factors because they tended to become negative), the conventional *R* value dropped to 3.1% for the 502 observed reflections. The following weights were applied: $w = 1$ for $F_0 < 80$ and $w = 80/F_0$ for $F_0 \ge 80$; i.e., the used weights varied between 1.0 and 0.30 *(Food*) $= 648$, $F_{\text{min}} = \sim 7$). None of the unobserved reflections was calculated greater than *Fmn.* The ratio of shifts to the given esd values was less than 0.23 in the final least-squares cycle, the average for this ratio being 0.033. For the refinements the **ORFLS** program of Busing, Martin, and Levy⁴ was used (incorporated in the "X-Ray 70 System" running on the IBM 370/145 computer of our department at the University of Marburg). The following atomic form factors were **used:** Te, K⁺, F⁻, and O^{6,7} and H_{bond}.⁸ No anomalous scattering was taken into consideration for Te (neither for the other atoms).

Description and Discussion of the Structure

As can be seen from the lattice constants, from Table I, and from Figure 1, the structure can be idealized to a cubic one with space group Pa3 (with $a = 9.042$ Å; Te at 0, 0, 0; K⁺ and F⁻ at *x*, *x*, *x* with $xK = 0.231$ and $xF = 0.397$; O at 0.203, $0.041, -0.037$. Further idealization, omitting the fluorine ions, leads to the structure type of K2PtC16 (space group Fm3m; K at $1/4$, $1/4$, $1/4$; Cl at x, 0, 0). To make space for the F⁻ ions, all Te(OH)6 octahedra are to be turned somewhat out of these ideal positions. It is difficult to find an obvious reason for the fact that for the real structure the symmetry reduction does not stop at space group Pa3 but goes down to Pcab. The main reason may be a somewhat less favorable coordination of the potassium ions in space group Pa3: $1 F$ ⁻ at \sim 2.60 Å, 3 O at \sim 2.78 Å, 3 O at \sim 2.98 Å, and eventually 3 O at \sim 3.36 Å, i.e., a coordination number of 7 or 10 in the hypothetical cubic space group, whereas in the real orthorhombic structure the coordination number of K^+ is 10 (8 O and 2 F ; see Table 11). We are preparing the analogous rubidium compound to see whether this is cubic or not. Heating of the potassium compound in a Guinier camera caused no convergence of the three lattice constants to a unique value, but the compound decomposed at 110 ± 2 °C as already reported by Kolditz and Fitz.1

The $Te(OH)$ 6 octahedron is nearly ideal: the $Te-O$ distances vary between 1.902 and 1.911 Å (average 1.905 Å; see

 $\frac{1}{2}$ **1 x**, **y**, $\frac{1}{2}$ **z** *z*, $\frac{1}{2}$ *z*, $\frac{1}{2}$ *x*, $\frac{1}{2}$ *x*, $\frac{1}{2}$ *y*, $\frac{1}{2}$ *z*, $\frac{1}{2}$ *z*, $\frac{1}{2}$ *z* d^{2} d^{2} d^{2} f^{2} f^{2

Table **III.** Bond Valences v^a in Te(OH) $\cdot 2KF^b$

^a In vu (valence units).¹¹ $b L(K-0) = (1.82-1.10 \log \nu)$ A, $L(Te-O) = (1.905-0.80 \log v)$ \overrightarrow{A} , $L =$ bond length from Table II. The bond valences involving H are estimated from the F. * **.O** distances. Distances to F are handled as 0.04 A longer distances to 0.

Table II; in Te(OH) $_6$ ·NaF², Te-O = 1.91 and 1.92 Å, each three times) and the angles O–Te–O between 88.4 and 91.6° (because of the **f** symmetry the other 3 angles are exactly 180'). The *O--O* edges of the octahedron are 2.66-2.73 **A.** For comparison the mean Te-0 distance in the monoclinic form of telluric acid is 1.916 **A** (x-ray data9) and 1.909 **A** (neutron data 10), respectively.

All three independent OH groups are involved in short 0-H-F hydrogen bonds of about 2.58 **A,** by which threefourths of the charge of the fluorine ion is already compensated resulting in a K-F bond of 2.59 **A,** which is scarcely shorter than in potassium fluoride itself $(2.673 \text{ Å}, \text{bond valence } 1/6)$. In $Te(OH)_{6}$ NaF only three out of the six OH groups are involved in O-H--F hydrogen bonds, but these are even somewhat shorter $(O - F = 2.50 \text{ Å})$. In Table III the bond valences¹¹ are estimated. The valence sums indicate how well a charge compensation is achieved for all ions: the additional bonding of the OH groups to the potassium ion is compensated by a weakening of the **0-H** bonds. The fluorine ion acts as a good acceptor for the now necessary hydrogen bonds. With the (rather inaccurate) hydrogen positions determined here, the three O-H_I-F angles are 175, 161, and 159°, respectively. The bond angles around the 0 and F ions are given in Table IV .

A quantum chemical calculation for H_2O-F^- by Kistenmacher et al.12 (LCAO-SCF Gaussian base) yielded similar

Figure 1. Projection of the crystal structure of Te(OH)₆.2KF onto the *x*, *y* plane $(x, 0^{-1/2}; y, 0^{-1})$. The octahedra around $z = 0$ are drawn with double lines; those around $z = \frac{1}{2}$, with single lines. Not all H atoms are given. The eight neighbors (O only) of one K are given by stippled lines.

Figure 2. Ir and Raman spectra of Te(OH)₆.2KF: —, ir spectrum in Nujol, KBr windows (below 500 cm⁻¹, CsJ windows); N = Nujol bands; \cdots , ir spectrum in polyfluoroethylene (somewhat shifted upward); \cdots , Raman spec

dimensions as found in this structure: $O \cdot F = 2.52$ Å and $O-H...F = 173^{\circ}$ for the most stable configuration (23.5) kcal/mol) or 2.55 **A** and 180' for a linear hydrogen bond (23.4 kcal/mol). As usual the 0-H distances found here are too short as compared with the calculated ones $(O-H = 1.00 \text{ Å})$. Therefore in Table III the bond valences involving H are directly derived from the more accurate O.F distances. In contrast to these O-H-F bonds F-H-O hydrogen bonds are even shorter, e.g., $F \cdot \cdot O = 2.38$ Å in K[PHO₂(OH)] \cdot HF.¹³

The coordination of the oxygen ions up to $L_{\text{max}}(K-\text{O})$ = 3.33 **8,** is somewhat different as indicated in Table IV. The sums \sum 3 of the three angles L-O-L' formed with the nearest three ligands are 358.9, 359.7, and 347.5° for $O(1)$, $O(2)$, and 0(3), respectively, perhaps indicating a different hybridization: more sp² for $O(1)$ and $O(2)$ and more sp³ for $O(3)$ (and F).

Infrared and Raman Spectra

Because of the centrosymmetry $(C_i = \overline{1})$ of the Te(OH)₆ complex in the structure at hand, the ir and Raman spectra cannot coincide. Altogether the following normal vibrations are to be expected

As is seen in Figure 2, the ν (TeO) bands between 700 and 600 cm-' are very sharp and strong and, in both spectra, are split threefold as expected (Raman 644 (vs), 624 (5), and 609 (m) cm⁻¹; for ir wavenumbers see Figure 2). The δ (TeO) bands are in the range $305-380$ cm⁻¹ (Raman 380 (s), 370 (m, sh), 360 (m, sh, *2),* and 326 (m) cm-1). The lines originating in the OH groups are completely missing in the Raman spectrum; at small wavenumbers only some lattice vibrations show up at 176 (w) and 155 (mw) cm⁻¹. On the contrary, these lines are well resolved in the ir spectrum. **As** the three independent OH groups are involved in somewhat different O-H-F hydrogen bonds (O-F = 2.537, 2.590, and 2.605 A, respectively), each of the three kinds of bands should

Table IV. Angles L-O-L' (deg, above the Diagonal) and Distances between the Ligands (A, below the Diagonal) around the O and F Ions in Te(OH) $_6^{\circ}$ -2KF

 $a_1/2 - x$, y , $-1/2 + z$, $b_1-1/2 + x$, $1/2 - y$, z , c_2x , $-1/2 + y$,
 $1/2 - z$, $d_1/2 - x$, y , $1/2 + z$, $e_1/2 - x$, $-1/2 + y$, $-z$, $f_2 - x$, $-1/2 + z$, $g_1/2 + y$, $1/2 - z$, $h_1/2 + x$, $h_2 - y$, z .

be split threefold. For $\nu(OH)$, however, only one very broad band is found at 2720 cm⁻¹. This corresponds¹² to an $O-H \cdots O$ bridge of about 2.63 Å; i.e., because of the \sim 0.04 Å smaller ionic radius of F⁻ this bond indicates an O-H_{**}F bridge of about 2.59 Å. This expected value agrees well with the found mean O-F distance of 2.58 Å.

The δ (TeOH) band (in plane) is somewhat structured: 1160 (s) cm⁻¹ with a shoulder at 1190 cm^{-1} . The latter value should correspond to the shortest O-H_"F bridge, whereas the other two O.F distances differ too little. Because of the anharmonicity of these vibrations the first overtones also appear at wavenumbers 2250 (m) and 2370 (w) cm⁻¹, which are not quite doubled.

The γ (TeOH) band (out of plane) is rather nicely split into three lines at 935 (m), 890 (m), and 815 (mw) cm^{-1} , which do not coincide with the $v(TeO)$ band as in the case of $Te(OH)$ and $Te(OH)$ 6 NaF .

The valence band $\nu(OH - F)$ corresponding to the hydrogen bonds shows up at 255 cm⁻¹ as for $Te(OH)6$ -NaF.

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Supplementary Material Available: Listing of structure factor amplitudes (1 page). Ordering information is given on any current masthead page.

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Contribution from the Chemistry Department, University of Virginia, Charlottesville, Virginia 22901

Crystal Structure of a Mixed-Ligand Complex of Copper(II), 1,10-Phenanthroline, and Glycylglycine Dianion: Glycylglycinato(1,10-phenanthroline)copper(II) Trihydrate

M. C. LIM,ⁱ EKK SINN,^{*} and R. BRUCE MARTIN^{*}

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The crystal and molecular structures of glycylglycinato(1,10-phenanthroline)copper(II) trihydrate has been determined by single-crystal x-ray diffraction, using counter methods. In the mixed Cu(II) complex glycylglycine serves as a terdentate ligand with amino, ionized amide nitrogen, and carboxylate oxygen donor atoms approximately tetragonally disposed about $Cu(II)$. The fourth tetragonal position about $Cu(II)$ is occupied by one phen nitrogen atom while the other more distant nitrogen occupies a tilted apical position resulting in an overall distorted square-pyramidal geometry about Cu(II). The individual complex molecules are hydrogen bonded to their neighbors via the three water molecules, forming a polymeric hydrogen-bonded lattice. Visible absorption spectra results suggest that the structure found in the crystal persists in aqueous solution near pH 9. Crystal data: CuO6N4C16H20, space group PI, $Z = 2$, $a = 7.842$ (1) Å, $b = 9.395$ (2) Å, $c = 13.763$ (4) Å, $\alpha = 74.64$ (2)°, $\beta = 72.00$ (2)°, $\gamma = 75.76$ (2)°, $\bar{V} = 915$ Å³, $R = 3.1\%$, 1664 reflections.

After amide nitrogen deprotonation, glycylglycine dianion (gg) serves as a terdentate ligand with amino, ionized amide nitrogen, and carboxylate oxygen donor atoms about tetragonal $Cu(II)$. Originally deduced from potentiometric titrations,² this structure, which exists in neutral aqueous solutions^{3,4} has been confirmed by optical⁵ and calorimetric⁶ results in solution

and by an x-ray study in a crystal, where water molecules occupy the fourth position in the tetragonal plane and an axial position.⁷ Due to the planar amide bond, terdentate gg with an ionized amide nitrogen never assumes a bent but only the planar conformation about a transition metal ion. In an aqueous solution study of mixed complexes of oligoglycines