atom thermal motion along the equatorial Cu–N bonds in the static phase of $M_2PbCu(NO_2)_6$ compounds. Since the effect of the lone pair on Pb^{2+} is not seen in the corresponding $K_2PbNi(NO_2)_6$ structure, it is not important enough to affect a non-Jahn–Teller ion similar in size to Cu^{2+}. However, it does appear to be of sufficient importance to influence the type of Jahn–Teller distortion in $M_2M'Cu(NO_2)_6$ compounds.

The other difference between Pb^{2+} and alkaline earth ions is the greater tendency of Pb^{2+} to form covalent bonds. Electronic spectral data provide evidence for electron transfer from Pb^{2+} to the $Cu(NO_2)_6{}^{4-}$ unit.[33] However, the Pb–O bond is too long for covalent contributions to have an important effect on $Cu(NO_2)_6{}^{4-}$ geometry. In our opinion, the most important cause of the pseudocompressed tetragonal $Cu(NO_2)_6{}^{4-}$ is the stereochemical activity of the lone pair of electrons on Pb^{2+}.

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Registry No. $K_2PbCu(NO_2)_6$, 15291-22-2.

Supplementary Material Available: A listing of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of $Te_5O_4F_{22}$: *trans*-$F_2Te(OTeF_5)_4$[1]

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Crystals of $Te_5O_4F_{22}$ are tetragonal, space group $I4_1/a$, with $a = 9.816$ (2) Å, $c = 20.341$ (6) Å, $Z = 4$, $d_{\text{calcd}} = 3.795$ g cm^{-3}, and $V = 1959.9$ Å^3. The refinement for 1178 unique reflections (diffractometer data, $F^2 > \sigma(F^2)$) with anisotropic temperature factors for all atoms converged to $R = 0.048$. The structure is built up by $TeF_2(OTeF_5)_4$ molecules, which have $\bar{4}$ symmetry imposed by the lattice. The central tellurium is bonded to four oxygen atoms of the $OTeF_5$ groups and two fluorine atoms in trans position. The bond angles on all tellurium atoms deviate only slightly from the octahedral symmetry. Average bond distances are Te–F = 1.808 (5) Å for the $OTeF_5$ group, Te–F = 1.849 (8) Å for the central octahedron, and Te–O = 1.875 (5) Å.

Introduction

The compound $Te_5O_4F_{22}$ is a minor product of the reaction of $As(OTeF_5)_3$ with elemental fluorine[2] or, as was found later, a product of the fluorination of $Te(OTeF_5)_4$.[3] Among all known oxide fluorides of Te(VI), it is the only one solid at room temperature, mp 72 °C. The stoichiometry $Te_5O_4F_{22}$ allows many structural isomers, and even with the general rules for the bonding in oxide fluorides of Te(VI) that no Te–O double bonds occur and that the environments around all tellurium atoms are octahedral, there are still 12 isomeric molecules possible.[2] The compound $Te_5O_4F_{22}$ follows these general rules. As already described in a short communication,[4] the molecule obtains high symmetry, in fact the highest possible of all structural isomers.

Experimental Section

Tellurium(VI) tetrakis[oxopentafluorotellurate(VI)] difluoride was prepared as described earlier.[2,3] Although the crystals were almost moisture insensitive they were sealed in glass capillaries for the x-ray measurements. The cell parameters were determined from precession photographs and refined with the indexed lines of a Guinier film (Cu Kα_1 radiation, λ 1.54051 Å, quartz monochromator, calibration substance $Pb(NO_3)_2$, $a = 7.856$ (1) Å). The space group is determined

Table I. Atomic Parameters and Anisotropic Temperature Factors,[a] Standard Deviation in Parentheses, for *trans*-$F_2Te(OTeF_5)_4$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Te(1)	0.0	0.25	0.125	2.43 (2)	2.43	3.70 (3)	0	0	0
Te(2)	0.28774 (4)	0.04476 (5)	0.09631 (3)	2.77 (2)	3.56 (2)	4.46 (2)	0.29 (1)	0.17 (2)	−0.97 (2)
F(1)	0.0	0.25	0.0341 (3)	4.76 (30)	5.12 (31)	4.00 (27)	−0.60 (24)	0	0
F(2)	0.4162 (5)	0.0987 (6)	0.1543 (3)	3.64 (20)	6.97 (30)	7.98 (31)	1.21 (20)	−2.02 (19)	−2.56 (24)
F(3)	0.3628 (6)	0.1518 (7)	0.0344 (3)	7.46 (3)	8.88 (36)	6.47 (29)	−2.86 (29)	3.33 (25)	−0.63 (28)
F(4)	0.2139 (6)	0.9342 (5)	0.1579 (3)	7.43 (31)	3.49 (19)	5.65 (26)	−0.40 (18)	−0.22 (21)	0.64 (18)
F(5)	0.1589 (5)	0.9864 (5)	0.0385 (2)	4.78 (21)	5.82 (24)	4.82 (21)	−0.98 (19)	−0.17 (18)	−1.78 (19)
F(6)	0.3970 (6)	0.9071 (7)	0.0700 (4)	5.00 (25)	7.20 (31)	11.48 (43)	1.93 (24)	0.46 (28)	−4.65 (30)
O	0.1813 (5)	0.1909 (5)	0.1267 (3)	2.58 (17)	3.43 (19)	5.80 (26)	0.16 (15)	−0.06 (18)	−0.77 (19)

[a] The form of the temperature factor is $\exp[-0.25(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

unambiguously by the extinctions (hkl for $h + k + l = 2n + 1$, $hk0$ for $h = 2n + 1$, $00l$ for $l + 1$). The intensities were collected on a STOE Weissenberg diffractometer (graphite monochromator, Mo Kα radiation, λ 0.7107 Å), using the ω scan technique with a scan rate of 1.2°/min and background measurements for 25 s on both sides of the reflection. The scan ranges for the reflections of the first four layers $hk0$–$hk3$ were constant (3°), and the scan ranges for the higher layers were calculated by the formula $\Delta\omega = A + B \sin \mu/\tan \theta'$ (where θ' is half the angle between counter and horizontal plane, μ is the equi-inclination angle, and A and B are constants, which had to be determined and had values of about 2°). For the layers $hk0$–$hk26$ 1387 unique reflections were measured with a crystal rotating about the c axis. The crystal had approximately the dimensions 0.13 × 0.20 × 0.30 mm. During the intensity measurements (12 days) six equatorial reflections were examined daily. The decrease was almost uniform and the scattering was not greater than the accuracy of the measurement. The intensities decreased slowly down to 80% of the original values, and the reflections of each layer were scaled according to this decrease. For 209 of the measured reflections σ_I was greater than the intensity I ($\sigma_I = (Z + 0.0009I^2)^{1/2}$, where Z is the total count of the scan and the background measurements). These reflections were considered unobserved and not included in the refinement. Lorentz–polarization and absorption corrections were applied to the data (range of absorption corrections 0.222–0.342).

Crystal Data: Formula $Te_5O_4F_{22}$, mol wt 1119.95, tetragonal, space group $I4_1/a$ (No. 88); $a = 9.816$ (2) Å, $c = 20.341$ (6) Å, $V = 1959.9$ Å^3, $Z = 4$, $d_{calcd} = 3.795$ g cm^{-3}, and $\mu_{Mo\ K\alpha} = 75.8$ cm^{-1}.

Structure Determination. The structure was solved by Patterson and Fourier syntheses and refined by least-squares methods minimizing $\sum w(|F_o| - |F_c|)^2$. The weight w was set equal to $1/\sigma_F^2$, where $\sigma_F = 0.5\cdot\sigma_I/(Lp\cdot I)^{1/2}$. The refinement with anisotropic temperature factors for all atoms converged to $R_1 = \sum|\Delta F|/\sum|F_o| = 0.050$ and $R_2 = [\sum w(F)^2/\sum wF_o^2]^{1/2} = 0.048$ for observed reflections. Scattering factors by Cromer and Mann were used,[5] and the dispersion correction for tellurium was included.[6] In the last cycle 12 individual scale factors were refined to compensate the decrease of the crystal. One scale factor was introduced for two consecutive layers, respectively, and for three in the case of higher layers, as the number of reflections becomes relatively small for these layers. The refinement gave only slightly better R values, $R_1 = 0.049$ and $R_2 = 0.047$. The final parameters are listed in Table I.

Structure Description and Discussion

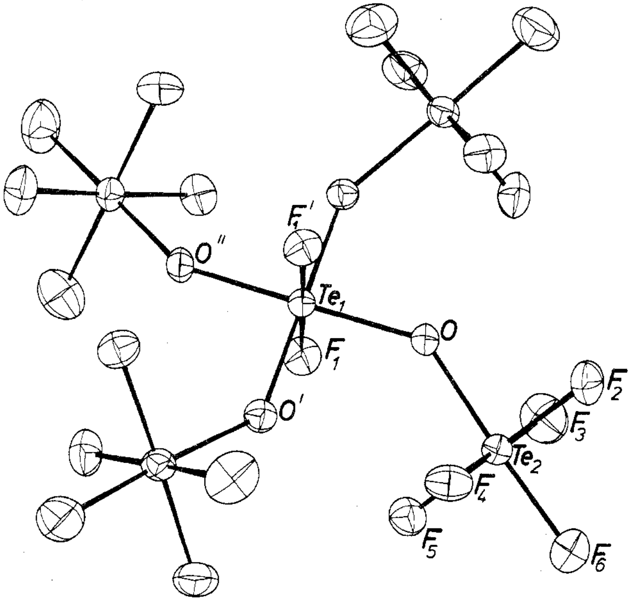

Figure 1. *trans*-$F_2Te(OTeF_5)_4$ molecule. The thermal ellipsoids are scaled to 25% probability.

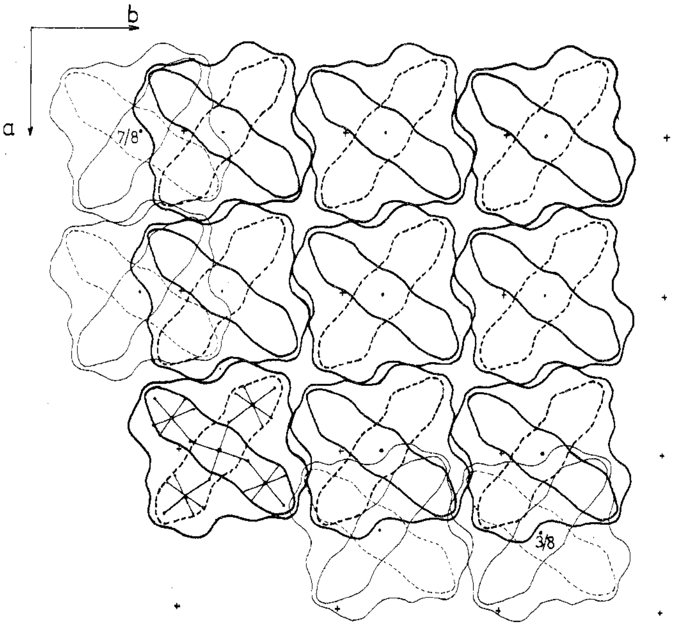

Figure 2. Packing diagram of a layer of $Te(OTeF_5)_4F_2$ disks projected on the ab plane with the central Te atom in $z = {}^1/_8$. Dashed lines indicate diagonal ridges on the lower side. Upper and lower layers are drawn lightly. Dots represent the central tellurium atoms and crosses the cell corners.

The crystal structure is built up by isolated $TeF_2(OTeF_5)_4$ molecules. The molecule lies in a special position with the central tellurium atom in the rotary inversion center and the two fluorine atoms of the central octahedron on the rotary inversion axis. The molecule has therefore $\bar{4}$ symmetry. The central tellurium atom Te(1) is surrounded by two fluorine atoms and four $OTeF_5$ groups in a nearly regular octahedral arrangement with the fluorine atoms in trans position. The four oxygen atoms deviate only slightly from the plane perpendicular to the F(1)–Te(1)–F(1)′ axis, with the TeF_5 groups pointing alternately up and down. The tellurium atom Te(2) of the $OTeF_5$ group has also a nearly regular octahedral coordination. The angles around Te(1) and Te(2) deviate by a maximum of 4° from the octahedral angles. The whole molecule can approximately be described as a square plate. The two TeF_5 groups and the fluorine atom on the same side of the TeO_4 plane pack to generate a well-defined diagonal ridge on that side of the molecule. A similar ridge, but at a right angle to the other one, lies on the other side of the

Table II. Bond Distances (Å) and Angles (deg), Standard Deviations in Parentheses

Te(1)-F(1)	1.849 (8)	Te(2)-F(4)	1.810 (5)
Te(1)-O	1.872 (5)	Te(2)-F(5)	1.819 (5)
Te(2)-F(2)	1.806 (5)	Te(2)-F(6)	1.806 (5)
Te(2)-F(3)	1.798 (6)	Te(2)-O	1.879 (5)
F(1)-Te(1)-F(1)′	180	F(3)-Te(2)-F(5)	90.9 (3)
F(1)-Te(1)-O	88.9 (2)	F(3)-Te(2)-F(6)	89.2 (3)
O-Te(1)-O′	90.0 (1)	F(3)-Te(2)-O	90.7 (3)
O-Te(1)-O″	177.9 (4)	F(4)-Te(2)-F(5)	88.9 (3)
F(2)-Te(2)-F(3)	90.0 (3)	F(4)-Te(2)-F(6)	89.7 (3)
F(2)-Te(2)-F(4)	90.2 (3)	F(4)-Te(2)-O	90.4 (3)
F(2)-Te(2)-F(5)	178.7 (3)	F(5)-Te(2)-F(6)	89.2 (3)
F(2)-Te(2)-F(6)	89.9 (3)	F(5)-Te(2)-O	93.8 (3)
F(2)-Te(2)-O	87.1 (2)	F(6)-Te(2)-O	177.0 (3)
F(3)-Te(2)-F(4)	178.9 (3)	Te(1)-O-Te(2)	139.4 (3)

molecule. The molecules are arranged in layers parallel to the *ab* plane with the F(1)–Te(1)–F(1)′ axis perpendicular to the *ab* plane. The layer above (beneath) is shifted by 0.5*a* in the direction of the *a* axis (*b* axis), so that their centers lie in the hollows between the molecules of the first layer.

The molecules pack such that the ridges of adjacent molecules lie parallel. This arrangement gives good packing and explains why this is so far the only tellurium(VI) oxide fluoride solid at room temperature. The very recently synthesized *cis*-$F_2Te(OTeF_5)_4$ is in fact a liquid at room temperature.[3] All intermolecular distances are longer than the sum of the van der Waals radii in question. The Te–F distances in the $OTeF_5$ group lie between 1.80 and 1.82 Å and are shorter than in the central octahedron Te(1)–F(1) = 1.85 Å. The similarity of the Te–F distances in the $OTeF_5$ group and their difference from the distance Te(1)–F(1) suggest that the different coordination of the two tellurium atoms has some unknown influence on the Te–F distances.

In $U(OTeF_5)_6$,[7] the only other known structure with $OTeF_5$ groups, the temperature factors are very high and the distances are strongly affected by the thermal motion. The corrected values for the Te–F vary by ±0.06 Å and the mean value 1.86 (4) Å is somewhat greater than in this structure. Two structure determinations of gaseous TeF_6 give slightly different values: 1.86 (1)[8] and 1.824 (4)[9] Å. All known Te–F distances for Te(VI) compounds lie in the range from 1.80 to 1.86 Å and are shorter than in Te(IV) compounds (1.86–2.01 Å)[10–13]. The distances Te(1)–O and Te(2)–O are almost equal, but they are larger than in $U(OTeF_5)_6$,[7] 1.81 Å (not corrected for thermal motion).

The angle of 139.4 (3)° at the oxygen atom deviates significantly from expected values like 109 or 120°. Similar values are found in some other Te–O compounds.[14] A simple explanation for this effect is the repulsion between Te(1) and Te(2), which would otherwise come into too close contact.[15] On the other hand in $H_2Te_2O_3F_4$[13] the two tellurium atoms are also connected by an oxygen atom. The Te–O distance 1.919 (6) Å is only slightly greater, but the angle at the oxygen is some 20° smaller than in $Te(OTeF_5)_4F_2$. It can be assumed that in $Te(OTeF_5)_4F_2$ because of the high valency state of Te a considerable $(p\text{–}d)_\pi$ bonding mechanism is the reason for this high angle value. This angle is only exceeded by the TeOTe angle in $F_5Te\text{–}O\text{–}TeF_5$ (145°), as was found recently by electron diffraction.[16]

Registry No. *trans*-$F_2Te(OTeF_5)_4$, 60788-81-0.

Supplementary Material Available: A listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Preparation and Characterization of Pyrrole-*N*-carbodithioate Complexes of Selected Transition Elements[1]

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The preparation and characterization of selected transition element complexes of the pyrrole-*N*-carbodithioate ligand (L) are reported. Specifically bis complexes with Cu(II), Cd(II), Pt(II), Pd(II), and Co(II) as well as a tris complex with Fe(III) have been isolated. A mixed chloride–ligand complex of Pt(IV), $PtCl_2L_2$, was also prepared. Infrared spectra of the metal complexes indicate an exocyclic single C–N bond, as opposed to other dithiocarbamate ligands. Computer analysis of the proton NMR spectra of the complexed and uncomplexed ligand indicates little positive charge buildup on the heterocyclic nitrogen atom, consistent with the infrared data. An electron spin resonance study of the Cu(II) complex yielded the following spin Hamiltonian parameters: $g_\parallel = 2.11$, $g_\perp = 2.02$, $A_\parallel = 144.8 \times 10^{-4}$ cm^{-1}, $A_\perp = 30.5 \times 10^{-4}$ cm^{-1}, $\langle g \rangle = 2.07$, and $\langle a \rangle = 62.2 \times 10^{-4}$ cm^{-1}. These data, when considered with the optical transition for this complex, are consistent with a very covalent σ and π metal–sulfur bond. These results when taken together illucidate the predominate electronic structure of the complexed ligand as being somewhat unique among dithiocarbamate systems.

Introduction

Since the first report by Cambi and co-workers over 35 years ago of the unusual properties of iron dithiocarbamate complexes,[2] a great deal of interest has centered on various examples of these ligand systems.[3–6] Our interest in dithiocarbamate complexes arises from our extensive investigation of the effects of resonance structures of the dianion of cyclopentadienedithiocarboxylic acid on the electronic structure of coordinated metals[7–12] as depicted below. The results of this study clearly indicate that the driving force toward an aromatic five-membered ring creates a dominant π-accepting character at the sulfur atom and produces some unusual