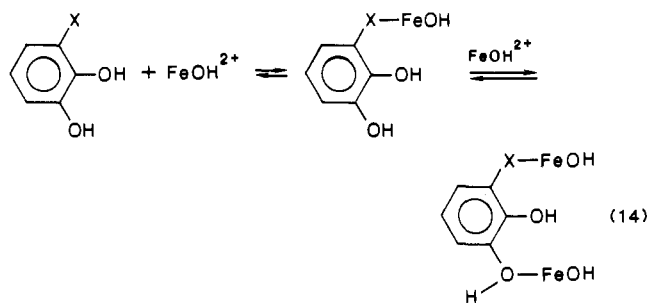


$\times 10^{-3}$) = 5, and for $[H^+] = 0.7$ M, $k_3 \ll 7$ M $^{-1}$ s $^{-1}$ for the protonated ligands.

The assignment of the $FeOH_2^{3+}$ + carboxylate anion reactions remains ambiguous, and the probable associative activation^{20,21} makes comparisons between ligands much less meaningful. The apparently similar rate constants for the DHB $^-$ and salicylate anions with $FeOH_2^{3+}$ seems reasonable, but all of this reactivity could be assigned to $FeOH^{2+}$ with the protonated ligand as discussed above.

The observation that the complexing of Tiron, DHB, and DHB $^-$ contains a term second order in $[Fe^{3+}]$ and essentially inverse second order in $[H^+]$ remains to be discussed. As well as being unusual in itself, it is also noteworthy that this kinetic term is not apparent in the complexing of catechol or salicylate. The implication is that the $[Fe^{3+}]^2$ dependence is enhanced or perhaps requires substituents in the 1- and 3-positions of the aromatic ligand. Elimination of either the 1-OH (salicylate) or 3-CO $_2$ H (catechol) suppresses or eliminates this kinetic path. One explanation for the $[Fe^{3+}]^2$ dependence could be in terms of eq 14.

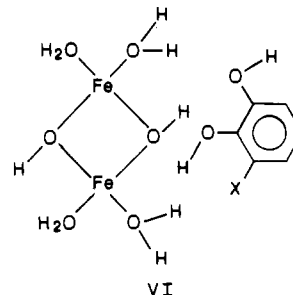


This possibility seems unlikely in view of the limited complexing ability of $-SO_3^-$ and $-CO_2H$. Furthermore, it is not at all obvious why the addition of the second $FeOH^{2+}$ in eq 14 should be competitive with intramolecular rearrangement of the monoiron(III) complex to products.

An explanation of the $[Fe^{3+}]^2$ term may be formulated in terms of the iron(III) dimer, which is the third most abundant iron species in solution.^{23,24} This dimer has been taken to have a

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bis(μ -hydroxy) structure from potentiometric and NMR relaxation data²⁴ and from kinetic evidence.²⁵ However, recent spectroscopic studies^{26,27} on much more concentrated solutions have been interpreted to indicate a μ -oxo structure. It may be relevant to note that $Cr(OH_2)_6^{3+}$ produces a bis(μ -hydroxy) species in dilute acid,²⁸ although the μ -oxo species can be made by other methods. Whatever the structure is, the iron(III) dimer may form a particularly reactive precursor complex when the appropriate ligand substituents are present. The structure may be represented by VI or an analogous form for the μ -oxo structure. The polar



substituents at positions 1 and 3 on the ligand provide the possibility of simultaneous interaction with both iron(III) centers to stabilize the precursor complex to substitution. After substitution on one iron, the dimer presumably would dissociate rapidly.²⁹

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support, and J.X. thanks the Peking Medical College for a study leave and financial support.

Registry No. III, 303-38-8; IV, 77310-82-8; Fe^{3+} , 20074-52-6.

Supplementary Material Available: Listings of kinetic results for the reaction of iron(III) with Tiron and DHB (3 pages). Ordering information is given on any current masthead page.

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Notes

Contribution from the Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2

$(Et_3Te^+Ag_4I_5^-)_n$: Synthesis and X-ray Structure of a Layered Polyanion

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Organotellurium salts containing a halide or a halogen-rich anion such as MX_4^- or MX_6^{2-} ($M = B(III), Al(III), Sb(III), Te(IV), Sn(IV), Ti(IV)$; $X = F, Cl, Br$) are well-known.^{1,2} In an attempt to prepare a salt with a dithiophosphate anion from Et_3TeI and $Ag^+[S_2P(OEt)_2]^-$, the compound $(Et_3Te^+Ag_4I_5^-)_n$ was

obtained in good yield. X-ray structural analysis reveals that the structure has some interesting differences from those of the alkali-metal or ammonium salts, which belong to a class of $Ag-I$ -based solid electrolytes.^{3,4} These differences can be ascribed to the $Te \cdots I$ secondary interionic interactions.

Experimental Section

The silver salt of *O,O*-diethyl dithiophosphate (1.72 g, 5.85 mmol) was prepared from equimolar aqueous solutions of $AgNO_3$ and $NH_4^+[S_2P(OEt)_2]^-$ and reacted in situ with an aqueous solution of 2.00 g (5.85 mmol) of Et_3TeI , prepared as described earlier.² The reaction mixture was warmed up to 70 °C for ca. 3 h and cooled to room temperature, and the yellow oil that formed as a result of the reaction was separated from the reaction mixture with CH_2Cl_2 . The solution was concentrated, and $CHCl_3$ was added to it. A dull yellow crystalline product gradually separated from the solution. (Anal. Found: C, 5.19; H, 0.99. Calcd for $C_6H_{15}TeAg_4I_5$: C, 5.62; H, 1.17. Mp 155–160 °C; yield 0.75 g, 50%.) An X-ray structural analysis of a single crystal showed the com-

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Table I. Summary of Crystal Data, Intensity Collection, and Structural Refinement for $(\text{Et}_3\text{TeAg}_4\text{I}_5)_n$

$a/\text{\AA}$	12.334 (5)
$b/\text{\AA}$	21.315 (7)
$c/\text{\AA}$	8.333 (3)
β/deg	104.0 (3)
cell vol/ \AA^3	2126 (1)
cryst syst	monoclinic
space group	$P2_1/c$
mol wt	1281.2
$Z, F(000)$	4, 2224
cryst dimens/mm	$0.12 \times 0.26 \times 0.50$
abs coeff μ/cm^{-1}	114.04
min abs cor	3.598
max abs cor	13.021
Mo $K\alpha$ radiation, $\lambda/\text{\AA}$	0.71069
monochromator	highly oriented graphite
temp/ $^\circ\text{C}$	20 ± 1
2θ angle/deg	4–45
scan type	coupled $\theta(\text{cryst})/2\theta(\text{counter})$
scan width/deg	$K\alpha_1 - 1$ to $K\alpha_2 + 1$
scan speed/deg min $^{-1}$	variable, 2.02–4.88
bkgd time/scan time	0.5
total no. of rflns measd	3039 (+ h , + k , $\pm l$)
no. of unique data used	1905 [$I > 3\sigma(I)$], $R_{\text{av}} = 0.0695$
no. of params (NP)	115
R^a	0.059
R_w^b	0.066
error in observn of unit wt	1.80
$\Delta\rho_{\text{max}}/e \text{\AA}^{-3}$	3.1
shift:error (max)	0.02

$$^a R = (\sum ||F_o| - |F_c|| / \sum |F_o|). \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}.$$

pound to be $\text{Et}_3\text{Te}^+\text{Ag}_4\text{I}_5^-$. The thick yellow oil left behind was analyzed to be a mixture of *O,O,S*-triethylthiophosphoric acid (m/z 214, relative abundance 40%) and Et_3Te (m/z 217, relative abundance 17% based on ^{130}Te) by mass spectrometry. The spectrum was obtained on a VG-7070 EHF double-focusing mass spectrometer operating at 70 eV.

The crystal used for X-ray analysis was sealed in a capillary tube, and data were collected on a Syntex $P2_1$ diffractometer. Details concerning collection and reduction of data and sources of scattering factors and computer programs used have been previously reported.⁵ Unit cell parameters were determined from 15 reflections having $15 < 2\theta < 30^\circ$. Three intensity standards were measured every 60 reflections, and no significant decay of the data was observed. The data were corrected for Lorentz and polarization effects, and an analytical absorption correction was applied with use of ABSORB. Systematic absences ($h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$)) indicate the space group $P2_1/c$. The structure was solved by direct methods using the programs SHELX and MULTAN. Of the 10 highest peaks of approximately the same height in the E map, the peak that had three ethyl groups attached to it was taken as the tellurium atom. Three peaks that were found to be at a distance somewhat less than 4.35 \AA (the van der Waals distance between Te and I) from the Te atom were taken as iodine atoms. Four atoms were found to have transannular contacts in the range 3.14–3.45 \AA . These atoms were taken to be silver atoms. Finally, the remaining two peaks were assumed to be iodine atoms. This assignment was confirmed, as any other choice of I, Te, and Ag atoms among the 10 peaks would give a slightly higher R factor in the final cycle of refinement. The structure was refined by full-matrix least-squares methods minimizing the quantity $\sum w(|F_o| - |F_c|)^2$. A weighting scheme of the form $1/[\sigma^2(F) + pF^2]$ was employed with a final p value of 0.0001. The I, Te, and Ag atoms were refined anisotropically and C atoms isotropically. Hydrogen atoms were not included in the calculations. A few peaks on the order of 2–3 $e \text{\AA}^{-3}$ were found in the final difference map. Following the successful refinement of the structure the model was tested for the diffusion of silver ions through the iodine network. The residual electron density peaks at a distance of 0.8–2.2 \AA from iodine atoms were included as the partially populated silver atoms,⁶ the site occupancy factors of the $\text{Ag}(1)\text{--Ag}(4)$ and $\text{I}(1)\text{--I}(5)$ atoms being allowed to vary at the same time. It was observed that only one position (coordinates 0.396, 0.159, and 1.114 distances 0.88, 2.75, and 2.75 \AA from $\text{Ag}(4)$, $\text{I}(3)$, and $\text{I}(4)$, respectively) represented some significant amount ($\sim 6\%$) of the electron density required for a silver atom, and the site occupancies of $\text{Ag}(1)\text{--Ag}(4)$ and

Table II. Final Fractional Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms of $(\text{Et}_3\text{TeAg}_4\text{I}_5)_n$ with Standard Deviations in Parentheses

	x	y	z	$U_{\text{eq}}^a/U, \text{\AA}^2 \times 10^3$
I(1)	0.4068 (1)	0.2472 (1)	0.8372 (2)	49 (1)
I(2)	0.0589 (1)	0.2060 (1)	0.4964 (2)	64 (1)
I(3)	0.2050 (1)	0.0860 (1)	0.9733 (2)	57 (1)
I(4)	0.5851 (1)	0.0927 (1)	1.1114 (2)	58 (1)
I(5)	0.3919 (2)	0.0642 (1)	0.5347 (2)	71 (1)
Te	0.7365 (1)	0.0816 (1)	0.7627 (2)	62 (1)
Ag(1)	0.1776 (2)	0.2093 (1)	0.8395 (3)	71 (2)
Ag(2)	0.2869 (2)	0.1778 (1)	0.5457 (3)	77 (2)
Ag(3)	0.3977 (2)	0.0421 (1)	0.8714 (3)	81 (2)
Ag(4)	0.3897 (2)	0.1293 (1)	1.2159 (4)	93 (2)
C(1)	0.662 (3)	0.169 (2)	0.685 (5)	126 (14)
C(2)	0.729 (3)	0.221 (2)	0.658 (5)	120 (14)
C(3)	0.882 (3)	0.121 (2)	0.931 (4)	119 (13)
C(4)	0.905 (3)	0.100 (2)	1.099 (5)	123 (14)
C(5)	0.825 (4)	0.074 (3)	0.572 (5)	147 (17)
C(6)	0.881 (4)	0.017 (4)	0.579 (7)	176 (22)

^a U_{eq} values for iodine, silver, and tellurium atoms are calculated from the refined anisotropic thermal parameters ($U_{\text{eq}} = 1/3 \sum \sum U_{ij} a_i^* a_j^* a_i a_j$).

Table III. Selected Interatomic Distances (\AA) and Angles (deg) for $(\text{Et}_3\text{TeAg}_4\text{I}_5)_n$

I(1)–Ag(1)	2.944 (3)	I(5)–Ag(4 ^d)	2.991 (4)
I(1)–Ag(2)	2.922 (3)	Ag(1)···Ag(2)	3.140 (3)
I(1)–Ag(2 ^a)	3.002 (3)	Ag(2)···Ag(4 ^d)	3.451 (4)
I(1)–Ag(4 ^b)	2.810 (3)	Ag(3)···Ag(3 ^c)	3.400 (5)
I(2)–Ag(1)	2.881 (3)	Ag(3)···Ag(4)	3.442 (4)
I(2)–Ag(1 ^b)	2.835 (3)	Te–C(1)	2.11 (3)
I(2)–Ag(2)	2.807 (3)	Te–C(3)	2.16 (3)
I(3)–Ag(1)	2.843 (3)	Te–C(5)	2.14 (3)
I(3)–Ag(3)	2.869 (3)	C(1)–C(2)	1.43 (4)
I(3)–Ag(4)	2.811 (3)	C(3)–C(4)	1.43 (4)
I(4)–Ag(3)	2.876 (3)	C(5)–C(6)	1.40 (5)
I(4)Ag(3 ^c)	2.881 (4)	Te···I(3 ^c)	4.166 (6)
I(4)–Ag(4)	2.863 (4)	Te···I(4)	3.822 (6)
I(5)–Ag(2)	2.757 (3)	Te···I(5)	4.231 (6)
I(5)–Ag(3)	2.828 (3)	Te···I(5 ^f)	4.051 (6)
Ag(1)–I(1)–Ag(2)	64.7 (1)	Ag(2)–I(5)–Ag(3)	90.8 (1)
Ag(1)–I(1)–Ag(2 ^a)	62.2 (1)	Ag(2)–I(5)–Ag(4 ^d)	73.6 (1)
Ag(2)–I(1)–Ag(2 ^a)	122.0 (1)	Ag(3)–I(5)–Ag(4 ^d)	161.9 (1)
Ag(1)–I(1)–Ag(4 ^b)	105.7 (1)	I(1)–Ag(1)–I(2)	105.0 (1)
Ag(2)–I(1)–Ag(4 ^b)	101.3 (1)	I(1)–Ag(1)–I(2 ^a)	115.6 (1)
Ag(2 ^a)–I(1)–Ag(4 ^b)	72.8 (1)	I(2)–Ag(1)–I(2 ^a)	106.1 (1)
Ag(1)–I(2)–Ag(1 ^b)	104.3 (1)	I(1)–Ag(1)–I(3)	103.5 (1)
Ag(1)–I(2)–Ag(2)	67.0 (1)	I(2)–Ag(1)–I(3)	110.5 (1)
Ag(1 ^b)–I(2)–Ag(2)	66.0 (1)	I(2 ^a)–Ag(1)–I(3)	115.7 (1)
Ag(1)–I(3)–Ag(3)	102.3 (1)	I(1)–Ag(2)–I(1 ^b)	89.4 (1)
Ag(1)–I(3)–Ag(4)	88.7 (1)	I(1)–Ag(2)–I(2)	107.5 (1)
Ag(3)–I(3)–Ag(4)	74.6 (1)	I(1 ^b)–Ag(2)–I(2)	114.7 (1)
Ag(3)–I(4)–Ag(3 ^c)	72.4 (1)	I(1)–Ag(2)–I(5)	108.9 (1)
Ag(3)–I(4)–Ag(4)	73.7 (1)	I(1 ^b)–Ag(2)–I(5)	98.5 (1)
Ag(3 ^c)–I(4)–Ag(4)	108.3 (1)	I(2)–Ag(2)–I(5)	130.2 (1)
I(3)–Ag(3)–I(4)	104.8 (1)	I(1 ^a)–Ag(4)–I(4)	111.7 (1)
I(3)–Ag(3)–I(4 ^c)	111.5 (1)	I(3)–Ag(4)–I(4)	106.7 (1)
I(4)–Ag(3)–I(4 ^c)	107.6 (2)	I(3)–Ag(4)–I(5 ^e)	108.6 (1)
I(3)–Ag(3)–I(5)	114.5 (1)	I(4)–Ag(4)–I(5 ^e)	108.4 (1)
I(4)–Ag(3)–I(5)	116.8 (1)	I(1 ^a)–Ag(4)–I(5 ^e)	106.3 (1)
I(4 ^c)–Ag(3)–I(5)	101.5 (1)	I(1 ^a)–Ag(4)–I(3)	122.9 (1)
C(3)–Te–C(5)	91 (2)	C(1)–Te–C(5)	96 (2)
C(1)–Te–C(3)	95 (2)	Te–C(3)–C(4)	117 (3)
Te–C(1)–C(2)	120 (3)	Te–C(5)–C(6)	112 (4)

^a $x, 0.5 - y, 0.5 + z$. ^b $x, 0.5 - y, z - 0.5$. ^c $1 - x, -y, 2 - z$. ^d $x, y, z - 1$. ^e $x, y, 1 + z$. ^f $1 - x, -y, 1 - z$.

I(1)–I(5) varied between 0.90 (2) and 1.02 (2) with a slight decrease in $\Delta\rho_{\text{max}}$ to 2.0 $e \text{\AA}^{-3}$. Consequently, it was concluded that this structure has well-defined silver atom positions and the disorder of the Ag ions observed in RbAg_4I_3 and other Ag–I solid electrolytes^{6–8} is quite unlikely.

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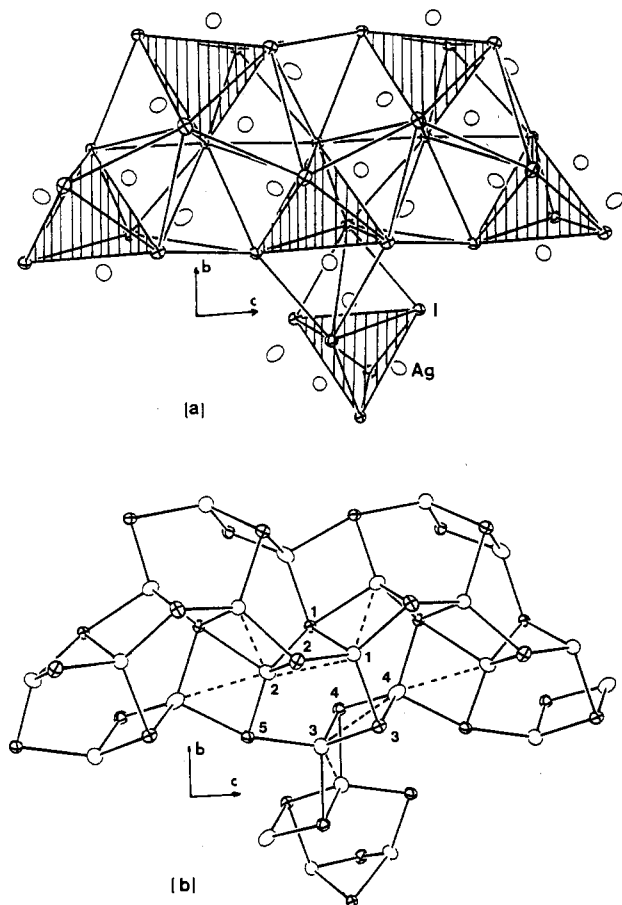
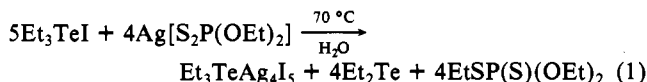


Figure 1. (a) Arrangement of I_5 trigonal bipyramids in a layer and the relative positions of the silver atoms in $(Ag_4I_5)_n^-$. (b) Arrangement with the I-I edges replaced by Ag-I bonds. The atoms are drawn with 20% probability ellipsoids. Ag...Ag interactions are shown by dashed lines.

The somewhat high value of the discrepancy indices and the inability to refine the carbon atoms anisotropically may be due to the absorption effects. Details of X-ray data and refinement parameters are summarized in Table I, and the final atomic coordinates for non-hydrogen atoms are given in Table II. The important distances and angles are recorded in Table III.

Results and Discussion

Et_3TeI and $Ag^+[S_2P(OEt)_2]^-$ react as shown by



If the reaction mixture is not warmed up to 70 °C for 3 h, unreacted Et_3TeI is recovered, and if instead the mixture is refluxed for longer periods, the products decompose to metallic Te, AgI, and $EtSP(S)(OEt)_2$. In any case, the intended $Et_3Te^+[S_2P(OEt)_2]^-$ could not be obtained.

When AgI and Et_3TeI in the molar ratio 4:1 were refluxed in $CHCl_3$ for 7 days, a small amount of a mixture of inseparable triethyltelluronium salts containing Ag_xI_{1+x} anions ($x = 1-5$) was obtained along with ~90% unreacted AgI. The formation of $Ag_xI_{1+x}^-$ ions was confirmed by FAB and negative ion mass spectrometry. It is therefore possible that reaction 1 proceeds in two steps. First, $Et_3Te[S_2P(OEt)_2]$ is formed, which then decomposes to Et_2Te and $EtSP(S)(OEt)_2$, and the other product AgI reacts with Et_3TeI to form the compound $Et_3Te^+Ag_4I_5^-$.

The 1H NMR spectrum of the title compound in $CDCl_3$ shows a triplet (1.58 ppm) and a quartet (2.84 ppm, $J = 7.5$ Hz) typical of an ethyl group. The mass spectrum shows Te-containing-cluster peaks for Et_3TeI^{+} (0.6%), Et_2TeI^+ (1.0%), $EtTeI^{+}$ (3.2%), TeI^+

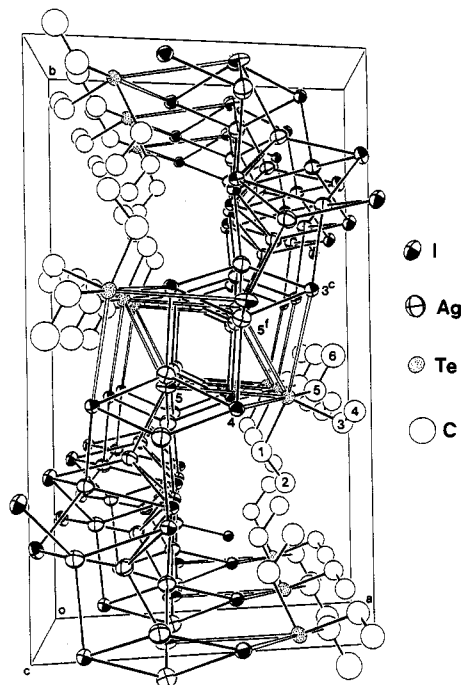


Figure 2. Unit cell packing diagram showing extension of a sheet of $(Ag_4I_5)_n^-$ in the yz plane. The Te...I secondary contacts are shown by open bonds. For symmetry-related positions, see the footnotes in Table III.

(1.0%) Et_2Te^{+} (51%), and Te^{+} (51%) and peaks for EtI^{+} (87%) and I_2^{+} (1.1%). No silver-containing fragment was observed.

The structures of $RbAg_4I_5$ and other Ag-I-based electrolytes are characterized by face-sharing iodine tetrahedra, which provide a network of passageways along which the Ag^+ ions are able to diffuse. Ag^+ ions are located in tetrahedral sites, and because there are many more sites than there are Ag^+ ions, these ions can move rapidly from one site to another. As a result of this diffusion, the Ag^+ ions are extensively disordered throughout the iodine lattice.^{3,4,6-8} The structure of $(Et_3Te^+Ag_4I_5^-)_n$ on the other hand, may be described as arising from infinite layers of slightly distorted trigonal bipyramids (two face-sharing tetrahedra) formed by the iodine atoms, I(1)-I(5), with their equatorial planes making an angle of 35° with the plane bc, as shown in Figure 1a. The lengths of the edges of a trigonal bipyramid vary between 4.54 and 5.05 Å. The space left between the trigonal bipyramids can be divided into face-sharing tetrahedra. Of the six possible tetrahedral sites surrounding a trigonal bipyramid, four are occupied by the silver atoms, which link the iodine atoms to form a layer of the polyanion (Figure 1b). The extension of the structure in the a direction is interrupted by weak Te...I secondary bonds between the iodine atoms of the anion and Et_3Te cations that are present above and below the $(Ag_4I_5)_n^-$ layers (Figure 2).

The silver atoms are all four-coordinated with various deviations from the ideal geometry. The average I-Ag-I angles around the Ag atoms are 108 (5), 108 (14), 110 (5), and 111 (6)°, respectively.⁹ The average Ag-I distance is 2.87 (6) Å, which is comparable to that found in the solid electrolytes, e.g., 2.86 Å in $RbAg_4I_5$,³ 2.85 Å in $Ag_{21}I_{25}^{2-}$,⁷ and 2.87 Å in $Ag_4I_6^{2-}$.⁸ Among the Ag-I bonds in the title compound, the longest bonds are formed by the four-coordinated I(1), the average being 2.93 (8) Å. The other iodine atoms are three-coordinated and form two acute (range 62.2 (1)-74.6 (1)°) angles and one obtuse (101.3 (1)-122.0 (1)°) angle, the variation for I(5) being large (73.6 (1)-161.9 (1)°).

The silver atoms Ag(1), Ag(3), and Ag(4) form two transannular contacts each, while Ag(2) forms three such contacts. These

(8) Coetzer, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1975, B31, 2115.

(9) Esd's in mean values have been calculated with the use of the Scatter formula $\sigma = [\sum(d_i - \bar{d})^2 / (N - 1)]^{1/2}$, where d_i is the i th and \bar{d} is the mean of N equal measurements.

contacts are depicted in Figure 2. The average Ag...Ag distance is 3.34 (14) Å, which is significantly shorter than the one observed in the cubane-like isomer of (Ph₃P)₄Ag₄I₄ (3.483 Å)¹⁰ but longer than the respective distance in (Ag₂I₃)_n¹¹ (3.045 Å).

The Et₃Te⁺ ion is normal; the Te-C distances and C-Te-C angles are all as expected.² There are four Te...I contacts, the shortest being 3.822 (6) Å (with I(4)) and the longest being 4.231 (6) Å (with I(5)). All these interactions are approximately linear with the Te-C bonds, as postulated for such interactions to be the secondary bond interactions.¹²

Acknowledgment. We are thankful to the University of Manitoba Research Grants Committee for the financial support of this work and to Prof. John E. Drake, Chairman, Department of Chemistry and Biochemistry, University of Windsor, for allowing the time to use the Syntex P2₁ diffractometer.

Registry No. Et₃TeI, 104746-44-3; Ag[S₂P(OEt)₂]₂, 1186-32-9; Et₃TeAg₄I₅, 113273-48-6; Et₂Te, 627-54-3; EtSP(S)(OEt)₂, 2524-09-6.

Supplementary Material Available: Tables of I...I distances, I...I...I, I...Te-C, Ag...Ag...Ag, and I-Ag...Ag angles, and anisotropic thermal parameters, an ORTEP plot of (Ag₄I₃)_n¹¹ showing all the symmetry-related positions, and a figure displaying the contents of the unit cell (5 pages); a table of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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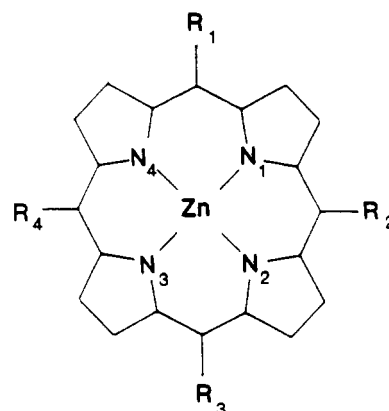
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Spin-Density Distributions in *meso*-Alkyl/Aryl Hybrid Porphyrin Cation Radicals

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Porphyrin cation radicals have been identified as intermediates in the catalytic cycles of a number of heme-containing peroxidases and catalases.¹⁻⁶ Cation radicals of pigments that are related to porphyrins also play an essential role in photosynthesis.⁷⁻¹² Consequently, considerable effort has been focused on the



	(CH ₂) ₄ CH ₃	p-(CH ₃ O ₂ C)- Φ
1:	R ₁ , R ₂ , R ₃ , R ₄	—
2:	R ₁ , R ₂ , R ₃	R ₄
3a:	R ₁ , R ₂	R ₃ , R ₄
3b:	R ₁ , R ₃	R ₂ , R ₄
4:	R ₁	R ₂ , R ₃ , R ₄
5:	—	R ₁ , R ₂ , R ₃ , R ₄

Figure 1. Atomic labeling scheme for the *meso*-alkyl/arylporphyrins.

characterization of these oxidized systems. Ring oxidation of a metalloporphyrin yields either a ²A_{2u} or a ²A_{1u} ground state; the specific ground state is determined by the nature of the ring substituents and/or the axial ligands to the metal ion.¹³⁻¹⁶ Molecular orbital calculations indicate that the unpaired charge density in a ²A_{2u} cation resides primarily on the pyrrole nitrogen and *meso*-carbon atoms whereas this density in a ²A_{1u} cation resides primarily on the pyrrole α - and β -carbon atoms.^{17,18} The resulting spin-density distributions in the two types of cations have been probed in detail by Fajer and co-workers who examined a number of β - and *meso*-substituted porphyrin cation radicals via electron paramagnetic resonance (EPR) techniques.¹⁶⁻¹⁸ These studies allowed the characterization of subtle variations in spin density as a function of the nature of the substituent group.

Previous EPR studies have primarily focused on porphyrin cations whose substituents are symmetrically disposed about the *meso*- or β -positions of the ring.^{14,17,19,20} The limitation of these studies to symmetrical systems is in large part due to the difficulty of preparing in good yield and high purity porphyrins that are asymmetrically substituted at the periphery of the macrocycle. Recently, one of our groups has developed a methodology which allows ready access to porphyrins that are asymmetrically *meso*-substituted (hybrid porphyrins).^{21,22} The basic synthetic strategy can also be used to enhance the efficiency of preparation of other exotic *meso*-substituted porphyrins such as isotopically labeled species. The availability of these various systems affords the opportunity to probe more systematically and in greater detail

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