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Crystal and Molecular Structures of the (4-Alkoxyphenyl)tellurium(IV) Trihalides (4-EtOPh)TeCl$_3$, (4-EtOPh)TeBr$_3$, and (4-MeOPh)TeI$_3$

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Single-crystal X-ray diffraction structure determinations have been performed on the trichloride, tribromide, and triiodide of (alkoxyphenyl)tellurium(IV). The crystal data are as follows: for (4-ethoxyphenyl)tellurium trichloride ((4-EtOPh)TeCl$_3$), space group orthorhombic, $P2_1am$, $a = 13.427$ (3) Å, $b = 11.767$ (2) Å, $c = 7.425$ (1) Å, $V = 1173.12$ Å^3, $Z = 4$; for (4-ethoxyphenyl)tellurium tribromide ((4-EtOPh)TeBr$_3$), space group triclinic, $P\bar{1}$, $a = 10.280$ (4) Å, $b = 11.029$ (8) Å, $c = 11.715$ (6) Å, $\alpha = 71.92$ (5)°, $\beta = 102.01$ (5)°, $\gamma = 99.29$ (5)°, $V = 1121.71$ Å^3, $Z = 4$; for (4-methoxyphenyl)tellurium triiodide ((4-MeOPh)TeI$_3$), space group triclinic, $P\bar{1}$, $a = 10.846$ (5) Å, $b = 11.346$ (6) Å, $c = 11.165$ (8) Å, $\alpha = 102.27$ (3)°, $\beta = 93.06$ (3)°, $\gamma = 104.98$ (3)°, $V = 1288.3$ Å^3, $Z = 4$. The diffraction intensities, 1025 for the trichloride, 3136 for the tribromide, and 3914 for the triiodide, with $I < 3\sigma(I)$ were collected on a Picker FACS-1 diffractometer. The structures were solved by conventional Patterson, Fourier, and full-matrix least-squares refinement techniques. The trichloride ($R_F = 0.049$, $R_{wF} = 0.056$) crystallizes as a polymer propagated in the [010] direction with approximate square-pyramidal coordination of each tellurium which is linked to the next through a single bridging chlorine. Te–Cl(terminal) distances are 2.395 (6) and 2.397 (6) Å, while the Te–Cl(bridging) distances are 2.740 (5) and 2.757 (5) Å. The tribromide ($R_F = 0.063$, $R_{wF} = 0.054$) and the triiodide ($R_F = 0.047$, $R_{wF} = 0.050$) both crystallize with a dimeric molecular unit; the two approximately square-pyramidal tellurium coordination polyhedra are cis-fused through two bridging halogens. The dimeric units are further arranged in pairs, square pyramids base to base, the exact placement differing between the two compounds. Te–Br(terminal) distances range from 2.509 (3) to 2.548 (2) Å while Te–Br(bridging) distances range between 2.884 (2) and 2.992 (3) Å. Te–I(terminal) distances range from 2.776 (1) to 2.797 (1) Å while Te–I(bridging) distances range between 3.097 (1) and 3.192 (1) Å. Te–C(aryl) distances range between 2.09 (2) and 2.16 (3) Å among the three compounds.

Introduction

Structural studies on a variety of organotellurium compounds have revealed intermolecular bonding effects of various types and strengths. In organotellurium diiodides,[1-7] interactions of the type Te---I or I---I have been shown to be very pronounced whereas in corresponding bromides either a very weak effect[8] or complete absence[9] of such effects has been reported. In dimethyltellurium dichloride,[10] however, a fairly strong interaction between a tellurium atom of one molecule and one chlorine on each of two neighboring molecules has been described.

A relatively smaller number of aryltellurium trihalide structures have been reported. Fairly weak interactions between monomeric species are found in 2-biphenylyltellurium tribromide[11] and two crystalline modifications of 2-biphenylyltellurium triiodide.[12,13] Nevertheless a 1,2-cyclohexylene-bridged tellurium tribromide structure[14] displays essentially symmetrical bromine bridging. The compound (2-chloroethyl)tellurium trichloride[15] crystallizes as a polymer with the chain propagated through single chlorine bridges.

Other investigations on the state of aggregation of alkyl- and aryltellurium trihalides have involved principally molecular weight measurements[16] and vibrational spectroscopy.[17] Halogen-bridged dimers or higher polymers are inferred from both these studies, and the latter suggest that the tribromides may have more complex structures than the chlorides or iodides.

In this paper we report the structures of (4-ethoxyphenyl)tellurium trichloride ((4-EtOPh)TeCl$_3$), (4-ethoxyphenyl)tellurium tribromide ((4-EtOPh)TeBr$_3$), and ((4-methoxyphenyl)tellurium triiodide ((4-MeOPh)TeI$_3$).

Experimental Section

Preparations. (4-Ethoxyphenyl)tellurium trichloride was prepared following the procedure of Reichel et al.[18] The compound was crystallized as thin yellow plates by slow evaporation of a saturated solution in glacial acetic acid. The crystals were washed with a little dry toluene.

(4-Ethoxyphenyl)tellurium tribromide and (4-methoxyphenyl)tellurium triiodide were prepared from the corresponding trichlorides by reduction to the diorganoditelluride[18] and subsequent reoxidation with the appropriate halogen in carbon tetrachloride.[19] The compounds were recrystallized from glacial acetic acid. ((4-Ethoxyphenyl)tellurium triiodide did not produce satisfactory crystals.)

Crystallographic Data. The procedures used were similar for the three structures. In each case zero- and first-level Weissenberg and precession photographs were used to check crystal quality and provide preliminary space group and unit cell dimension information. Accurate unit cell data were obtained on a Picker-Nuclear FACS-1 diffractometer, by a least-squares procedure based on the setting angles of 12 carefully centered reflections. The 12 reflections were centered at both positive and negative 2θ values, and averaged 2θ, ω, χ, and ϕ angles were used in the refinement. Details are listed in Table IA. After data collection by the conventional θ–2θ scan technique, the data were corrected for background radiation to give raw intensities I and estimated standard deviations $\sigma(I)$. These were then corrected

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Table I. Experimental Data for X-ray Diffraction Studies

A. Crystal Parameters at ~20 °C, with $\lambda(\text{Mo K}\alpha) = 0.710\,69$ Å

	$(4\text{-EtOPh})TeCl_3$	$(4\text{-EtOPh})TeBr_3$	$(4\text{-MeOPh})TeI_3$
a, Å	13.427 (3)	10.280 (4)	10.846 (5)
b, Å	11.767 (2)	11.209 (8)	11.346 (6)
c, Å	7.425 (2)	11.715 (6)	11.165 (8)
α, deg	90.00	71.93 (5)	102.27 (3)
β, deg	90.00	102.01 (5)	93.06 (3)
γ, deg	90.00	99.29 (5)	104.98 (3)
V, Å^3	1173.12	1271.71	1288.30
cryst system	orthorhombic	triclinic	triclinic
space group	$P2_1am^b$ (C_{2v}^2, No. 26)	$P\bar{1}$ (C_i^1, No. 2)	$P\bar{1}$ (C_i^1, No. 2)
mol wt	355.08	488.44	615.44
Z	4	4	4
ρ_{calcd}, g cm^{-3}	2.011	2.598	3.173
ρ_{obsd}, g cm^{-3}	2.02 (2)	2.61 (2)	
μ, cm^{-1}	32.63	125.96	96.23
cryst dimens			
$(100) \rightarrow (\bar{1}00)$, mm	0.15	0.40	0.10
$(010) \rightarrow (0\bar{1}0)$, mm	0.05	0.20	0.12
$(001) \rightarrow (00\bar{1})$, mm	0.15	0.50	0.25
estimated transmission factors, %	65–80	10–20	30–50

B. Measurement of Intensity Data

radiation	Mo Kα
monochromator	highly oriented graphite $2\theta_{002} = 12.1°$
cryst to detector dist, mm	25
detector	scintillation counter and pulse height analyzer set for 100% Mo K peak
attenuators	Ni foil used for intensities $<10^4$ Hz
takeoff angle, deg	3.0
detector aperture, mm	4 × 4
scan type	coupled θ(cryst)–2θ(detector), 2.0°/min
scan length	$\Delta(2\theta) = (\text{base width} + 0.692 \tan\theta)°$

	$(4\text{-EtOPh})TeCl_3$	$(4\text{-EtOPh})TeBr_3$	$(4\text{-MeOPh})TeI_3$
rotation axis	[001]	[100]	[001]
reflctns measd	$+h,+k,+l$	$\pm h,\pm k,+l$	$\pm h,\pm k,-l$
min 2θ, deg	4	4	4
max 2θ, deg	45	45	50
scan base width, deg	2.3	2.7	2.70
std reflctns	800, 070, 008 (every 50 cycles)	600, 060, 008 (every 50 cycles)	$60\bar{1}$, $\bar{1}06$, $06\bar{2}$ (every 40 cycles)
variation of std, %	±3	±2	±2 (random)
reflctns collected	1294	3670	5093
reflctns where $I < 3\sigma(I)$	1024	3136	3914

C. Structure Refinements

	(4-EtOPh)-$TeCl_3$	(4-EtOPh)-$TeBr_3$	(4-MeOPh)-TeI_3		(4-EtOPh)-$TeCl_3$	(4-EtOPh)-$TeBr_3$	(4-MeOPh)-TeI_3
			Isotropic Refinement				
cycles to convergence^a	4	5	5	R_{wF}	0.075	0.113	0.128
R_F	0.070	0.135	0.119	GOF	3.826	8.121	6.562
			Anisotropic Refinement				
cycles to convergence^a	8	7	5	R_{wF}	0.056	0.054	0.050
R_F	0.049	0.063	0.042	GOF	3.178	3.981	2.661

[a] Convergence was considered to have been reached when all variables were shifting less than one-tenth of their standard deviations. [b] Nonstandard setting of $Pmc2_1$.

for attenuator factor, Lorentz, and polarization effects. A locally written program for the Concordia University C.D.C. Cyber 172/2 computer system was used. The formulas used were

$$I = N - Bt_s/t_b$$

$$\sigma(I) = [N - B(t_s/t_b)^2 + (0.02N)^2]^{1/2}$$

$$(Lp)^{-1} = (\sin 2\theta_s)(\cos^2 2\theta_m + 1)/(\cos^2 2\theta_m + \cos^2 2\theta_s)$$

N and B are the counts accumulated during the scan period t_s and background counting time t_b, respectively, while $2\theta_s$ and $2\theta_m$ are the diffraction angles at sample and monochromator crystals, these being in mutually perpendicular planes. Unscaled structure amplitudes F and their esd's $\sigma(F)$ were calculated as

$$F = (I/Lp)^{1/2} \qquad \sigma(F) = \sigma(I)/(2(Lp)F)$$

Data for the bromide and iodide, which are subjected to severe absorption effects, were corrected by using the general absorption correction program GNABS.[20] The crystal of the chloride was accidentally destroyed before it could be measured. Table IB contains more complete details pertaining to the data collection and processing for the three compounds.

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(20) With the use of a modified version of GNABS, a general absorption correction program by: Burnam, C. W. *Am. Mineral.* **1966**, *51*, 159.

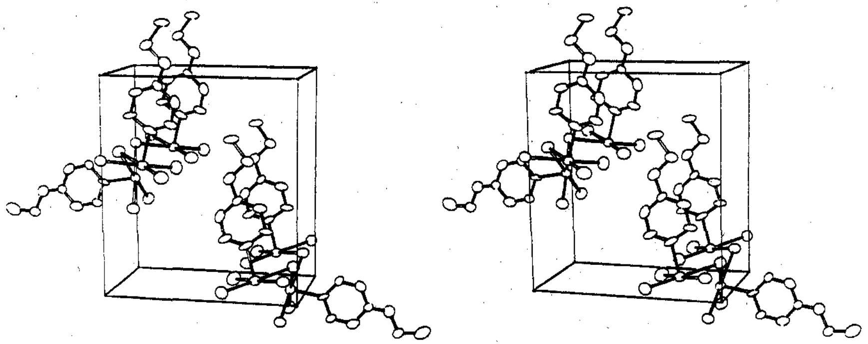

Figure 1. Unit cell packing of (4-EtOPh)$TeCl_3$ viewed approximately along the crystallographic *c* axis.

Structure Solution and Refinement. All three structures were solved by using conventional sharpened Patterson syntheses. Subsequent successful completion of the structure solutions and refinements confirmed the space group assignments. The map for the chloride yielded trial positions for two crystallographically independent Te atoms lying on mirror planes (Wyckoff positions a and b). The maps for bromide and iodide yielded trial positions for both Te and the halogen atoms. The remaining nonhydrogen atoms were located on Fourier syntheses phased by the trial heavy atoms. The structures were refined isotropically and then anisotropically by using "full matrices", except that computer memory restrictions necessitated the grouping of the atoms into two independent matrices at the anisotropic stage in the case of the iodide and the bromide structures.

The noncentrosymmetric trichloride was refined anisotropically as both enantiomorphs. The final results given in this paper correspond to the enantiomorph which gave the lower discrepancy indices: for the discarded enantiomorph the final values were $R_F = 0.056$ and $R_{wF} = 0.058$.

Scattering factors for neutral atoms were taken from the listings of Cromer and Waber[21] while corrections for the real and imaginary parts of the anomalous scattering by Te, Br, and I were taken from ref 22. Computer programs used during the structure solution and refinement included FORDAP by Zalkin for Patterson and Fourier synthesis and SFLS by Prewitt for structure factor and least-squares calculations. The drawings were prepared by Johnson's ORTEP. The function minimized in least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = [\sigma(F_o)]^{-2}$. The discrepancy indices listed in Table IC are $R_F = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$ and the "goodness of fit" (GOF) is $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, where *m* is the number of reflections included in the refinement and *n* is the number of variables refined. Final difference Fourier maps which were calculated at the end of refinement did not show any significant features. The final atomic parameters for the three structures are listed in Tables II–VII. The tables of observed and calculated structure factors are available (see paragraph at the end of paper regarding supplementary material).

Results and Discussion

(4-EtOPh)$TeCl_3$. Figure 1 depicts a stereographic view of the cell seen approximately down the *c* axis. The atom labeling is shown in Figure 2. Selected distances and angles are listed in Table VIII. The compound crystallizes as a chlorine-bridged polymer extended along the crystallographic *c* axis. Each tellurium atom has square-pyramidal coordination with the 4-ethoxyphenyl group in the apical position. The pyramids are linked in chains through cis basal chlorine atoms. This polymeric structure is essentially identical with that of $ClC_2H_4TeCl_3$.[15] In (4-EtOPh)$TeCl_3$ the terminal and bridging Te–Cl bond lengths average 2.396 and 2.749 Å, respectively, while the analogous distances in $ClC_2H_4TeCl_3$ are 2.386 and 2.717 Å, which are both slightly shorter. This difference can be rationalized given the more electron-releasing character of the 4-ethoxyphenyl group. Unfortunately the structure determinations are insufficiently accurate to permit significant

Table II. Final Positional Parameters[a] for (4-EtOPh)$TeCl_3$

atom	*x*	*y*	*z*
Te1	0.0000	−0.0849 (1)	−0.5000
Te2	−0.1069 (2)	−0.2151 (1)	0.0000
Cl1	0.1208 (5)	−0.1141 (4)	−0.2669 (8)
Cl2	−0.0779 (4)	−0.3515 (5)	−0.2335 (9)
Cl3	−0.1438 (4)	−0.0448 (4)	−0.2461 (7)
C11	0.0251 (18)	0.0901 (22)	−0.5000
C12	0.1263 (21)	0.1310 (23)	−0.5000
C13	0.1474 (22)	0.2461 (27)	−0.5000
C14	0.0670 (18)	0.3245 (22)	−0.5000
C15	−0.0299 (22)	0.2821 (26)	−0.5000
C16	−0.0534 (21)	0.1708 (22)	−0.5000
C17	0.1812 (23)	0.4816 (27)	−0.5000
C18	0.1728 (30)	6040 (37)	−0.5000
O1	0.0809 (17)	0.4328 (18)	−0.5000
C21	−0.2635 (23)	−0.2574 (30)	0.0000
C22	−0.2898 (24)	−0.3650 (29)	0.0000
C23	−0.3894 (27)	−0.3875 (24)	0.0000
C24	−0.4616 (22)	−0.2991 (23)	0.0000
C25	−0.4318 (21)	−0.1866 (29)	0.0000
C26	−0.3292 (18)	−0.1554 (27)	0.0000
C27	−0.6375 (26)	−0.2479 (32)	0.0000
C28	−0.7337 (25)	−0.3270 (36)	0.0000
O2	−0.5598 (17)	−0.3371 (20)	0.0000

[a] The estimated standard deviations in parentheses are right justified to the least significant digits of the fractional coordinates.

Table III. Final Thermal Parameters[a] for (4-EtOPh)$TeCl_3$

atom	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Te1	33 (1)	39 (1)	31 (1)	−4 (1)		
Te2	33 (1)	46 (1)	31 (1)	−2 (1)		
Cl1	53 (3)	59 (3)	57 (3)	−1 (3)	−24 (3)	6 (3)
Cl2	64 (4)	67 (3)	65 (4)	−3 (3)	19 (3)	−23 (3)
Cl3	47 (3)	56 (3)	43 (3)	1 (2)	11 (2)	10 (2)
C11	16 (16)	53 (17)	45 (15)	−15 (13)		
C12	28 (15)	38 (15)	56 (18)	−7 (13)		
C13	38 (17)	71 (22)	37 (16)	−8 (16)		
C14	29 (15)	33 (15)	37 (15)	−3 (12)		
C15	47 (17)	51 (18)	39 (16)	13 (14)		
C16	37 (16)	30 (14)	48 (17)	−7 (13)		
C17	37 (18)	45 (19)	65 (20)	−8 (15)		
C18	68 (26)	91 (29)	70 (26)	−29 (23)		
O1	53 (15)	51 (13)	64 (14)	0 (11)		
C21	33 (18)	69 (23)	80 (25)	−26 (18)		
C22	31 (16)	68 (21)	44 (17)	−19 (16)		
C23	67 (22)	36 (17)	72 (22)	−11 (17)		
C24	35 (16)	34 (15)	59 (19)	−12 (13)		
C25	27 (16)	73 (22)	72 (23)	6 (14)		
C26	16 (14)	70 (20)	58 (20)	5 (15)		
C27	36 (22)	51 (20)	140 (37)	10 (16)		
C28	21 (18)	83 (27)	142 (39)	−5 (20)		
O2	54 (15)	53 (14)	92 (18)	−12 (12)		

[a] The anisotropic parameters are applied in the expression $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)]$. The numbers in parentheses are the estimated standard deviations in the least significant digits.

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Table IV. Final Positional Parameters[a] for (4-EtOPh)$TeBr_3$

atom	x	y	z
Te1	0.2463 (1)	0.5073 (1)	0.2671 (1)
Te2	0.0823 (1)	0.3394 (1)	−0.0212 (1)
Br1	0.1967 (3)	0.4642 (3)	0.4795 (2)
Br2	0.4199 (2)	0.6899 (2)	0.2797 (2)
Br3	0.0368 (2)	0.3003 (2)	0.2231 (2)
Br4	0.2779 (2)	0.5496 (2)	0.0134 (2)
Br5	−0.0920 (2)	0.1579 (2)	−0.0488 (2)
Br6	0.1237 (2)	0.3936 (2)	−0.2395 (2)
C11	0.3852 (16)	0.3746 (14)	0.3249 (13)
C12	0.5019 (19)	0.4044 (17)	0.2774 (15)
C13	0.6058 (17)	0.3223 (17)	0.3227 (15)
C14	0.5835 (18)	0.2149 (16)	0.4222 (16)
C15	0.4650 (18)	0.1845 (17)	0.4686 (16)
C16	0.3663 (17)	0.2656 (16)	0.4193 (14)
C17	0.8225 (19)	0.1836 (22)	0.4605 (20)
C18	0.9042 (19)	0.1048 (25)	0.5573 (25)
O1	0.6825 (13)	0.1358 (11)	0.4799 (11)
C21	0.2376 (16)	0.2215 (14)	0.0528 (14)
C22	0.3547 (18)	0.2552 (16)	0.0006 (17)
C23	0.4621 (18)	0.1798 (15)	0.0517 (16)
C24	0.4472 (17)	0.0772 (15)	0.1538 (15)
C25	0.3316 (16)	0.0417 (14)	0.2021 (15)
C26	0.2236 (18)	0.1176 (16)	0.1522 (15)
C27	0.6774 (18)	0.0307 (18)	0.1641 (19)
C28	0.7611 (18)	−0.0712 (19)	−0.2467 (19)
O2	0.5504 (12)	0.0018 (11)	0.2122 (11

[a] The estimated standard deviations in parentheses are right justified to the least significant digits of the fractional coordinates.

Table V. Final Thermal Parameters[a] in (4-EtOPh)$TeBr_3$

atom	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Te1	57 (1)	47 (1)	44 (1)	9 (1)	3 (1)	−24 (1)
Te2	43 (1)	36 (1)	41 (1)	5 (1)	6 (1)	−18 (1)
Br1	121 (2)	136 (2)	52 (1)	45 (2)	18 (2)	−43 (2)
Br2	91 (2)	57 (2)	111 (2)	−2 (1)	−12 (2)	−49 (2)
Br3	51 (1)	61 (1)	50 (1)	4 (1)	19 (1)	−21 (1)
Br4	62 (2)	37 (1)	48 (1)	−9 (1)	12 (1)	−13 (1)
Br5	50 (1)	54 (1)	97 (2)	−6 (1)	3 (1)	−41 (1)
Br6	89 (2)	63 (1)	40 (1)	21 (1)	15 (1)	−14 (1)
C11	52 (12)	40 (10)	42 (10)	7 (9)	17 (9)	−20 (9)
C12	59 (14)	58 (13)	48 (12)	−10 (11)	11 (12)	−17 (10)
C13	46 (13)	64 (13)	45 (12)	−4 (11)	11 (9)	−8 (10)
C14	45 (13)	45 (12)	57 (12)	12 (10)	−6 (10)	−23 (10)
C15	31 (12)	66 (14)	64 (13)	3 (11)	−1 (10)	−20 (11)
C16	55 (13)	56 (12)	43 (11)	5 (10)	7 (9)	−23 (10)
C17	24 (12)	122 (20)	108 (18)	26 (13)	37 (13)	6 (16)
C18	25 (13)	155 (25)	158 (24)	4 (15)	1 (15)	−35 (21)
O1	75 (10)	64 (9)	64 (9)	8 (8)	7 (8)	−6 (8)
C21	48 (12)	26 (10)	42 (10)	2 (8)	11 (9)	−16 (9)
C22	55 (14)	43 (12)	74 (13)	1 (11)	17 (12)	−28 (10)
C23	67 (14)	26 (10)	56 (12)	12 (10)	19 (11)	−5 (9)
C24	36 (12)	29 (10)	59 (12)	3 (9)	6 (10)	−22 (9)
C25	32 (11)	29 (10)	59 (12)	1 (8)	15 (9)	−13 (9)
C26	70 (14)	34 (10)	47 (11)	−9 (10)	20 (10)	−19 (9)
C27	37 (13)	74 (15)	106 (17)	−6 (11)	40 (13)	−10 (14)
C28	37 (13)	85 (16)	114 (18)	38 (12)	−3 (12)	−26 (14)
O2	61 (9)	46 (8)	72 (9)	13 (7)	4 (7)	−15 (7)

[a] See footnote to Table III.

Table VI. Final Positional Parameters[a] for (4-MeOPh)TeI_3

atom	x	y	z
Te1	0.32481 (7)	0.17869 (7)	0.30642 (7)
Te2	0.67781 (7)	0.04317 (7)	0.38302 (7)
I1	0.12407 (8)	0.09294 (10)	0.11676 (9)
I2	0.22298 (9)	0.36708 (9)	0.42998 (9)
I3	0.43849 (8)	−0.03440 (7)	0.18214 (8)
I4	0.54237 (7)	0.23634 (7)	0.53161 (7)
I5	0.76911 (9)	−0.14199 (8)	0.24057 (8)
I6	0.87539 (8)	0.10037 (8)	0.57541 (8)
C11	0.4503 (10)	0.3018 (10)	0.2165 (10)
C12	0.5213 (11)	0.4160 (10)	0.2877 (11)
C13	0.6076 (11)	0.4962 (10)	0.2291 (12)
C14	0.6160 (11)	0.4602 (11)	0.1034 (11)
C15	0.5393 (11)	0.3462 (11)	0.0342 (11)
C16	0.4544 (11)	0.2649 (11)	0.0915 (11)
C17(Me)	0.7208 (14)	0.5095 (14)	−0.0708 (13)
O1	0.7014 (8)	0.5438 (8)	0.0578 (9)
C21	0.7754 (10)	0.1900 (10)	0.2986 (10)
C22	0.8311 (11)	0.3023 (11)	0.3693 (11)
C23	0.8946 (11)	0.4024 (10)	0.3132 (11)
C24	0.8969 (10)	0.3749 (10)	0.1899 (11)
C25	0.8355 (12)	0.2529 (11)	0.1143 (12)
C26	0.7732 (11)	0.1585 (11)	0.1688 (12)
C27(Me)	1.0025 (14)	0.5893 (11)	0.1901 (14)
O2	0.9514 (8)	0.4597 (7)	0.1243 (8)

[a] The estimated standard deviations in parentheses are right justified to the least significant digits of the fractional coordinates.

Table VII. Final Thermal Parameters[a] for (4-MeOPh)TeI_3

atom	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{12}	10^3U_{23}
Te1	33 (1)	35 (4)	34 (1)	11 (1)	1 (1)	6 (1)
Te2	36 (1)	33 (2)	40 (1)	12 (1)	7 (1)	11 (1)
I1	42 (1)	76 (1)	52 (1)	8 (1)	−16 (1)	3 (1)
I2	58 (1)	69 (1)	64 (1)	39 (1)	11 (1)	−5 (1)
I3	46 (1)	36 (1)	43 (1)	17 (1)	−1 (1)	1 (1)
I4	43 (1)	40 (1)	35 (1)	16 (1)	6 (1)	7 (1)
I5	60 (1)	40 (1)	53 (1)	27 (1)	13 (1)	8 (1)
I6	49 (1)	57 (1)	48 (1)	15 (1)	−6 (1)	14 (1)
C11	34 (6)	30 (6)	40 (7)	13 (5)	9 (5)	16 (5)
C12	48 (7)	32 (6)	44 (7)	19 (6)	6 (6)	11 (6)
C13	43 (7)	33 (6)	59 (8)	11 (6)	5 (6)	14 (6)
C14	33 (7)	43 (7)	53 (8)	20 (6)	7 (6)	18 (6)
C15	42 (7)	36 (7)	43 (7)	13 (6)	6 (6)	8 (6)
C16	49 (8)	48 (7)	36 (7)	28 (6)	6 (6)	7 (6)
C17	67 (9)	94 (12)	61 (10)	39 (8)	38 (8)	42 (9)
O1	47 (5)	55 (6)	74 (7)	12 (4)	18 (5)	76 (5)
C21	29 (6)	36 (6)	42 (7)	13 (5)	10 (5)	13 (5)
C32	37 (7)	40 (7)	51 (8)	18 (6)	13 (6)	5 (6)
C33	41 (7)	35 (6)	44 (7)	16 (6)	10 (6)	12 (6)
C34	33 (6)	35 (6)	55 (8)	19 (5)	17 (6)	13 (6)
C35	51 (8)	45 (7)	57 (8)	28 (6)	26 (6)	23 (6)
C36	40 (7)	56 (8)	59 (8)	27 (6)	14 (6)	20 (7)
C37	81 (10)	25 (7)	86 (11)	0 (7)	19 (9)	7 (8)
O2	69 (6)	45 (5)	62 (6)	13 (4)	24 (5)	22 (5)

[a] See footnote to Table III.

differences in Te–C bond orders to be observed which might support this hypothesis.

In both structures the tellurium atoms are found lying almost exactly in the basal planes formed by the four chlorine atoms: 0.004 and 0.029 Å below the plane relative to the aryl carbon atom in (4-EtOPh)$TeCl_3$ and 0.10 Å below this plane in $ClC_2H_4TeCl_3$. Angular distortions are such that the C–Te–Cl(bridging) angles are slightly smaller than C–Te–Cl(terminal) angles in both compounds: in (4-EtOPh)$TeCl_3$ these angles are 86.8 (5) and 89.6 (7)° and 91.8 (5) and 90.2 (7)°, respectively, while in $ClC_2H_4TeCl_3$ the difference is slightly larger: 82.5 vs. 92.7°.

Perhaps the most striking feature in both the trichloride structures is the quite acute angle between the basal planes of the pyramids. In (4-EtOPh)$TeCl_3$ this angle is 63.3°. This presumably results from weak bonding indicated by short distances between adjacent tellurium atoms, 4.265 (2) Å, and between one tellurium atom and terminal chlorines of the neighboring tellurium atoms, 3.854 (3) and 3.833 (3) Å. (The van der Waals contacts would be 4.4 and 4.0 Å, respectively.) A dibridged dimeric structure similar to the tribromide and triiodide molecules described below has been suggested for

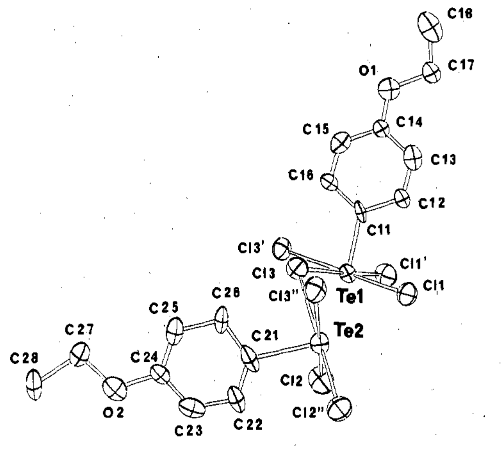

Figure 2. $(4\text{-EtOPh})TeCl_3$ atom labeling scheme.

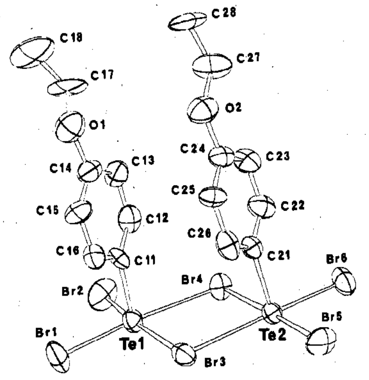

Figure 3. $(4\text{-EtOPh})TeBr_3$ dimer with atom labeling scheme.

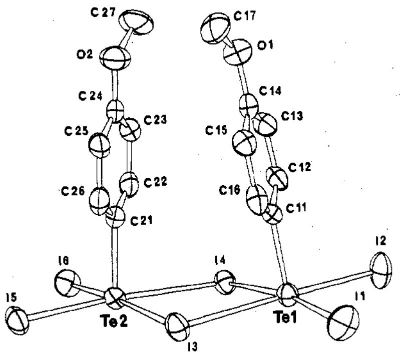

Figure 4. $(4\text{-MeOPh})TeI_3$ dimer with atom labeling scheme.

Table VIII. Bond Lengths (Å) and Angles (Deg) in $(4\text{-EtOPh})TeCl_3$

	Distances		
Te1–Cl1	2.397 (6)	Te2–Cl2	2.395 (6)
Te1–Cl3	2.740 (5)	Te2–Cl3	2.757 (5)
Te1–C11	2.09 (3)	Te2–C21	2.16 (3)
C11–C12	1.44 (5)	C21–C22	1.31 (7)
C12–C13	1.38 (5)	C22–C23	1.36 (6)
C13–C14	1.42 (6)	C23–C24	1.42 (6)
C14–C15	1.39 (5)	C24–C25	1.38 (5)
C15–C16	1.35 (6)	C25–C26	1.43 (6)
C16–C11	1.42 (5)	C26–C21	1.49 (7)
C14–O1	1.29 (5)	C14–O2	1.39 (6)
O1–C17	1.46 (6)	O2–C27	1.48 (7)
C17–C18	1.44 (6)	C27–C28	1.59 (7)
	Angles		
Te1–Cl3–Te2	101.8 (2)		
Cl1–Te1–Cl3	90.3 (2)	Cl2–Te2–Cl3	92.1 (2)
Cl1–Te1–Cl1	92.4 (2)	Cl2–Te2–Cl2″	92.8 (2)
Cl1–Te1–Cl3′	177.0 (2)	Cl2–Te2–Cl3″	175.1 (2)
Cl3–Te1–Cl3′	87.0 (2)	Cl3–Te2–Cl3″	83.0 (2)
Cl1–Te1–C11	91.8 (5)	Cl2–Te2–C21	90.2 (7)
Cl3–Te1–C11	86.8 (5)	Cl3–Te2–C21	89.6 (7)
C16–C11–C12	118 (1)	C26–C21–C22	128 (2)
C11–C12–C13	121 (2)	C21–C22–C23	117 (2)
C12–C13–C14	119 (1)	C22–C23–C24	122 (2)
C13–C14–C15	118 (2)	C23–C24–C25	120 (2)
C14–C15–C16	124 (2)	C24–C25–C26	122 (2)
C15–C16–C11	118 (2)	C25–C26–C21	111 (2)
Te1–C11–C12	119 (1)	Te2–C21–C22	119 (1)
Te1–C11–C16	123 (1)	Te2–C21–C26	113 (1)
C13–C14–O1	122 (1)	C23–C24–O2	114 (1)
C15–C14–O1	119 (2)	C25–C24–O2	125 (2)
C14–O1–C17	121 (2)	C24–O2–C27	116 (2)
O1–C17–C18	109 (2)	O2–C27–C28	99 (2)

$MeTeCl_3$[16] on the basis of molecular weight determination in solutions. Such a structure would probably be precluded by excessively short Te---Te or Cl---Cl distances across the four-membered bridged system.

The polymeric chains of the structure are packed together so that remaining contacts, which are at normal van der Waals distances, occur between the ethoxyphenyl moieties which are interleaved with others of neighboring chains and between ethoxyphenyl groups and the terminal chlorine atoms also on neighboring chains.

$(4\text{-EtOPh})TeBr_3$ and $(4\text{-MeOPh})TeI_3$. These two compounds present certain structural similarities and are discussed together. The coordination at tellurium is square pyramidal, with the halogen atoms in the basal positions and the organic group apical. The pyramids are linked in pairs by a shared basal edge, i.e., two virtually symmetrically bridging halogen atoms, and the aryl groups are cisoid. The dihedral angles formed by the pair of pyramid bases are 1.2 and 5.2° for the bromide and iodide, respectively. The structures of the dimeric

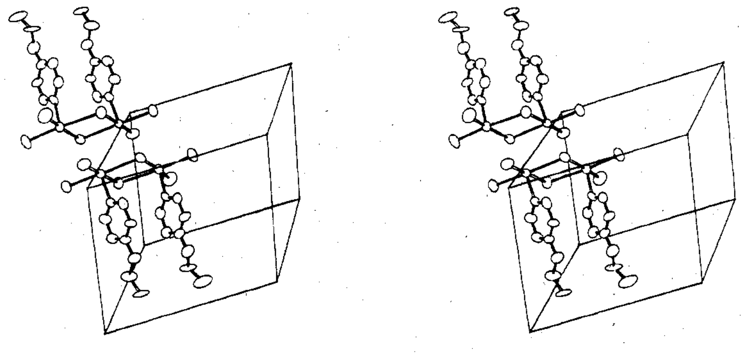

Figure 5. Unit cell packing of $(4\text{-EtOPh})TeBr_3$.

Table IX. Bond Lengths (Å) and Angles (Deg) in (4-EtOPh)TeBr$_3$ and (4-MeOPh)TeI$_3$

	(4-EtOPh)TeBr$_3$	(4-MeOPh)TeI$_3$		(4-EtOPh)TeBr$_3$	(4-MeOPh)TeI$_3$
		Distances			
Te1-X1	2.527 (3)	2.776 (1)	Te2-X3	2.884 (2)	3.146 (9)
Te1-X2	2.509 (3)	2.797 (1)	Te2-X4	2.912 (2)	3.177 (1)
Te1-X3	2.992 (3)	3.097 (1)	Te2-X5	2.539 (2)	2.783 (1)
Te1-X4	2.940 (3)	3.192 (1)	Te2-X6	2.548 (2)	2.797 (1)
Te1-C11	2.09 (2)	2.14 (1)	Te2-C21	2.11 (1)	2.16 (1)
C11-C12	1.38 (2)	1.37 (2)	C21-C22	1.41 (2)	1.32 (2)
C12-C13	1.43 (3)	1.42 (2)	C22-C23	1.41 (3)	1.45 (2)
C13-C14	1.42 (3)	1.39 (2)	C23-C24	1.39 (2)	1.35 (2)
C14-C15	1.39 (3)	1.38 (2)	C24-C25	1.37 (2)	1.43 (2)
C15-C16	1.38 (3)	1.41 (2)	C25-C26	1.42 (2)	1.39 (3)
C16-C11	1.39 (2)	1.37 (2)	C26-C21	1.38 (2)	1.41 (2)
C14-O1	1.38 (2)	1.35 (1)	C24-O2	1.39 (2)	1.36 (1)
O1-C17	1.49 (2)	1.45 (2)	O2-C27	1.48 (2)	1.44 (2)
C17-C18	1.41 (4)		C27-C28	1.50 (3)	
		Angles			
Te1-X3-Te2	93.56 (7)	94.47 (3)	Te1-X4-Te2	94.09 (7)	92.05 (3)
X1-Te1-X2	95.16 (10)	92.87 (4)	X3-Te2-X4	87.35 (7)	85.94 (3)
X1-Te1-X3	90.57 (9)	88.94 (4)	X3-Te2-X5	91.60 (8)	88.30 (3)
X1-Te1-X4	174.70 (9)	171.47 (4)	X3-Te2-X6	175.22 (8)	174.62 (4)
X2-Te1-X3	173.90 (9)	177.05 (4)	X4-Te2-X5	178.61 (8)	173.59 (4)
X2-Te1-X4	89.29 (8)	91.39 (3)	X4-Te2-X6	88.98 (7)	92.45 (3)
X3-Te1-X4	84.88 (6)	86.52 (3)	X5-Te2-X6	92.02 (8)	93.04 (3)
X1-Te1-C11	92.7 (4)	95.9 (3)	X3-Te2-C21	88.4 (4)	91.1 (3)
X2-Te1-C11	94.1 (4)	93.5 (3)	X4-Te2-C21	87.7 (4)	87.9 (3)
X3-Te1-C11	87.7 (4)	88.6 (3)	X5-Te2-C21	93.1 (4)	95.0 (3)
X4-Te1-C11	89.8 (4)	91.2 (3)	X6-Te2-C21	94.5 (4)	94.0 (3)
C16-C11-C12	121 (3)	123 (1)	C26-C21-C22	122 (2)	124 (1)
C11-C12-C13	121 (2)	117 (1)	C21-C22-C23	119 (2)	119 (1)
C12-C13-C14	116 (2)	120 (1)	C22-C23-C24	118 (2)	118 (1)
C13-C14-C15	123 (2)	120 (1)	C23-C24-C25	123 (2)	122 (1)
C14-C15-C16	118 (2)	120 (1)	C24-C25-C26	119 (2)	119 (1)
C15-C16-C11	121 (2)	118 (1)	C25-C26-C21	121 (2)	117 (1)
Te1-C11-C16	120 (1)	119 (1)	Te2-C21-C26	120 (1)	117 (1)
Te1-C11-C12	118 (1)	117 (1)	Te2-C21-C22	118 (1)	119 (1)
C13-C14-O1	121 (2)	115 (1)	C23-C24-O2	121 (1)	125 (1)
C15-C14-O1	116 (2)	125 (1)	C25-C24-O2	115 (1)	113 (1)
C14-O1-C17	118 (1)	118 (1)	C24-O2-C27	119 (1)	118 (1)
O1-C17-C18	105 (2)		O2-C27-C28	104 (2)	

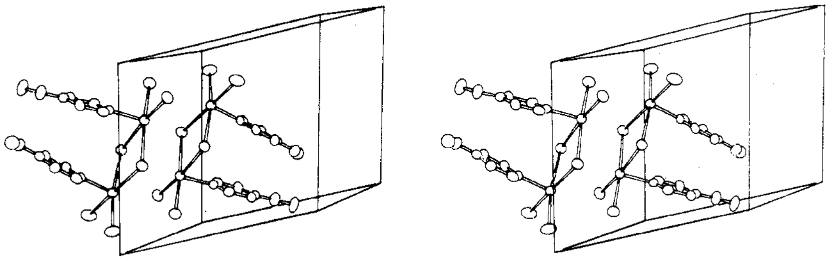

Figure 6. Unit cell packing of (4-MeOPh)TeI$_3$.

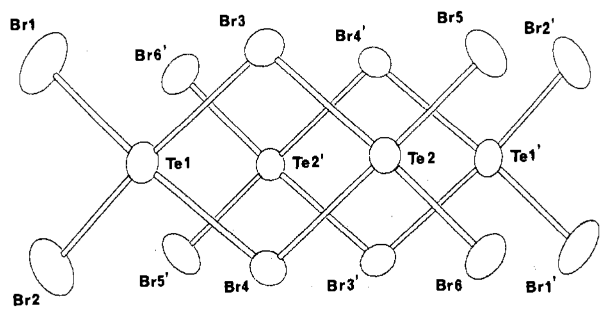

Figure 7. Juxtaposition of the basal planes of the dimers in (4-EtOPh)TeBr$_3$.

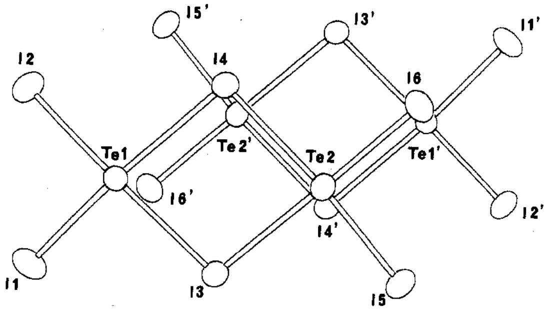

Figure 8. Juxtaposition of the basal planes of the dimers in (4-MeOPh)TeI$_3$.

trated in the packing diagrams, Figures 5 and 6. The bromide units, with atom labeling, are shown in Figures 3 and 4. The dimers are further associated, base to base, in pairs, as illustrated in the packing diagrams, Figures 5 and 6.

and iodide differ slightly in the relative positioning of the dimeric units. This is shown in Figures 7 and 8 which are projections perpendicular to a pair of basal planes. Corre-

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sponding distances and angles for the two compounds are collected in Table IX.

The dimers observed for the tribromide and triiodide reported here represent a structural type which seems uncommon, although vibrational spectroscopic studies[17] have led to the prediction of this type of association. The only X-ray determination of a structure which is similar is that of the 1,2-cyclohexylene-bridged $Te_2Br_6C_6H_{10}$, obtained from $TeBr_4$ and cyclohexene.[14] A survey of the nonionic dibromides, R_2TeBr_2,[8,9] and tribromides[11,14] shows these compounds to be essentially monomeric with weak but significant Te---Br interactions down to 3.591 Å[8] (cf. the van der Waals contact of 4.15 Å). The diiodides[1-7,23] and triiodides[12,13] show similar, but perhaps stronger Te---I interactions (between otherwise monomeric species) as short as 3.692 Å[3] and I---I distances as low as 3.239 Å[12] (cf. van der Waals contacts of 4.35 and 4.30 Å, respectively). By comparison, the analogous contacts between dimeric units in (4-EtOPh)$TeBr_3$ are very long: i.e., Te1---Br5′, 4.174 (2); Te1---Br6′, 4.054 (2); Te2---Br3′, 4.226; Te2---Br4′, 4.119 Å (representing only the slightest of interactions). Nevertheless, the Te1---Te2′ distance of 4.173 (2) Å is significantly less than the normal Te---Te van der Waals contact of 4.40 Å. In (4-MeOPh)TeI_3 the interdimer interactions appear stronger: the Te1---I6′ and Te2---I4′ distances are 3.874 and 3.779 Å, respectively, although Te1 and Te2 of the other dimer unit are not in contact. The interaction between the dimeric units is further manifested in the larger fold (see above) between the pyramid bases in the triiodide than in the tribromide, as a result of the weak bonding of the bridging iodines to a third tellurium atom. The molecule $Te_2Br_6C_6H_{10}$[14] which also possesses bridging halogen atoms reveals certain differences which might be ascribed to the constraint of the cyclohexylene group; thus, the dihedral angle between pyramid bases is approximately 53°, the Te–Br(bridging) distances are shorter (2.870 and 2.890 (8) Å) than those in (4-EtOPh)$TeBr_3$ (from 2.884 to 2.992 (2) Å), and, interestingly, there are quite short Br-Br intermolecular interactions of a type absent in (4-EtOPh)$TeBr_3$ [Br(terminal)---Br(terminal) down to 3.55 Å; Br(terminal)---Br(bridge) down to 3.59 Å (a normal Br---Br van der Waals contact is 3.90 Å)].

Terminal halogen to tellurium distances vary over a quite large range: from a low of 2.490 Å to a high of 2.675 Å for Te–Br and from 2.769 to 3.099 Å for Te–I in the trihalides alone. Such bonds are evidently easily deformed by inter- and intramolecular influences, but the literature contains too few examples for a detailed analysis. The bond distance observed in (4-EtOPh)$TeBr_3$, which ranges from 2.509 to 2.548 (2) Å, and those in (4-MeOPh)TeI_3, from 2.776 (1) to 2.797 (1) Å, are all within the previously observed limits.

Acknowledgment. This research has been supported by an operating grant awarded by the Natural Sciences and Engineering Research Council of Canada.

Registry No. (4-EtOPh)$TeCl_3$, 36310-31-3; (4-EtOPh)$TeBr_3$, 36310-32-4; (4-EtOPh)TeI_3, 36310-33-5; [(4-EtOPh)TeI_3]$_2$, 73597-13-4; [(4-EtOPh)$TeBr_3$]$_2$, 73611-44-6.

Supplementary Material Available: Tables of observed and calculated structure amplitudes (27 pages). Ordering information is given on any current masthead page.

Contribution from the Institute of Inorganic Chemistry, University of Fribourg,
CH-1700 Fribourg, Switzerland, and the Crystallography Laboratory, Oxford, Great Britain

Preparation of $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})X]^n$, a New Type of Cobalt(III)–Acidopentaamine Complex with a Dangling Amine, and the Crystal Structure of $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})Cl]Cl_3\cdot 2H_2O$

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The preparation of new acidopentaamine complexes, with the general formula $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})X]^n$ ($X = Cl^-, Br^-, OH^-, H_2O, SO_4^{2-}, SCN^-$; tame = 1,1,1-tris(aminomethyl)ethane), and their chemical and spectroscopic properties are reported. The complexes contain one terdentate and one bidentate tame, leaving one dangling amine. The crystal structure of $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})Cl]Cl_3\cdot 2H_2O$ has been determined to elucidate the configuration. This complex salt crystallizes in the space group $P2_1/c$, with $Z = 4$ ($a = 13.306$ (5) Å, $b = 9.777$ (2) Å, $c = 16.040$ (3) Å, $\beta = 101.73$ (2)°, $V = 2043.1$ Å^3). The structure has been refined to a final R_w of 0.092 from 2638 independent reflections. The hydrolysis of $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})Cl]^{3+}$ at pH 7.6–8.8 has been studied, and an acceleration due to the deprotonation of the dangling amine was observed.

Cobalt(III) complexes of partially coordinated polyamines are commonly postulated as reactive intermediates in isomerization and racemization reactions.[1,2] Only two complexes of this type have been reported in the literature, so far, to our knowledge. In a detailed study of Co^{III}penten complexes (*N,N,N′,N′*-tetrakis(β-aminoethyl)ethylenediamine) Schwarzenbach and Emmenegger[3] showed that, due to conformational strain in acid and base solutions, one chelate ring is opened and one primary amine group is replaced by a monodentate ligand. Alexander and Spillert[4] reported the preparation of $[Co(\eta^1\text{-Hen})(\eta^2\text{-en})_2X]^{3+}$, in which one en acts as a monodentate ligand. Preparing $[Co(\eta^3\text{-tame})_2]^{3+}$ from $Na_3Co(CO_3)_3\cdot 3H_2O$ and tame·3HCl (1,1,1-tris(aminomethyl)ethane) we always isolated in addition to the yellow hexaamine complex a red-violet byproduct. A slight modification of the reaction conditions allowed us to obtain the red-violet complex in yields higher than 60%. It was identified by chemical and spectroscopic methods as the acidopentaamine complex $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})Cl]^{3+}$ containing two tame, one acting as terdentate ligand and the other as a bidentate ligand, leaving a dangling amino group. Under these conditions the complex ion may have one of the two configurations shown in Chart I. Based on chemical and spectroscopic properties, it was not

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