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Synthesis, X-ray Crystal Structures, and NMR Spectroscopy of $[PPh_4]_2[M(Te_4)_2]$, M = Hg, Cd, Zn

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The compounds $[PPh_4]_2[M(Te_4)_2]$, M = Hg, Cd, Zn, have been prepared by reactions in DMF of appropriate metal salts with polytelluride solutions. X-ray crystal structure determinations were performed on single crystals of each compound. Crystal data for $[PPh_4]_2[Hg(Te_4)_2]$: tetragonal, $P\bar{4}$, $a = 21.365(3)$ Å, $c = 11.268(2)$ Å, $V = 5143$ Å^3, $R = 0.079$. Crystal data for $[PPh_4]_2[Cd(Te_4)_2]$: tetragonal, $I\bar{4}$, $a = 21.442(3)$ Å, $c = 11.259(2)$ Å, $V = 5176$ Å^3, $R = 0.045$. Crystal data for $[PPh_4]_2[Zn(Te_4)_2]$: tetragonal, $I\bar{4}$, $a = 21.396(4)$ Å, $c = 11.169(2)$ Å, $V = 5113$ Å^3, $R = 0.094$. These crystal structures are surprisingly complex, and the anions exhibit disorder; nevertheless, the anions have the expected structure of metal atoms coordinated tetrahedrally by two Te_4^{2-} chelates. ^{125}Te NMR spectra of these compounds and of $[PPh_4]_2[Pd(Te_4)_2]$ are reported, and assignments of metal-bound and ring-bound Te nuclei are given. The resulting trends in the ^{125}Te chemical shifts parallel those noted previously for the ^{77}Se chemical shifts in the selenometalate analogues.

Introduction

The chemistry of tellurometalates is expanding rapidly, and many new compounds were recently prepared that have no precedent among sulfido- or selenometalates.[1−5] Indeed, S or Se analogues of $[NbTe_{10}]^{3-}$,[6] $[AuTe_7]^{3-}$,[7] $[AgTe_7]^{3-}$,[8] $[HgTe_7]^{2-}$,[8,9] and $[ZnTe_7]^{2-}$ [9] are unlikely ever to be synthesized, because in these anions Te adopts nonclassical bonding modes unknown for S or Se. On the other hand, some tellurometalates have direct analogues among both sulfidometalates and selenometalates. As examples, the anions $[MO(Q_4)_2]^{2-}$, M = Mo, W, are known for Q = S, Se, and Te,[10−12] and the $[M(Q_4)_2]^{2-}$ anions are known for M = Ni, Pd, Zn, Hg and Q = S,[13−15] as well as for M = Ni, Pd, Zn, Hg, Pb, Cd, Mn and Q = Se,[16−20] where a general method of preparation has been reported.[20] Surprisingly, only the corresponding $[Pd(Te_4)_2]^{2-}$ species has been detailed.[21,22]

^{77}Se NMR spectroscopy has become a useful analytical tool in selenometalate chemistry,[10 20,23−26] but ^{125}Te NMR spectroscopy has not in tellurometalate chemistry owing to the paucity of data. In this paper we report syntheses, structural characterization, and ^{125}Te NMR spectra of $[PPh_4]_2[M(Te_4)_2]$ (M = Hg, Cd, Zn) and the ^{125}Te NMR spectrum of $[PPh_4]_2[Pd(Te_4)_2]$.

Experimental Section

Syntheses. All reagents were purchased from Aldrich Chemical Co., Milwaukee, WI, and used as received. Solvents were purchased from Baxter Scientific Products Inc., McGaw Park, IL. DMF (analytical reagent) was distilled from CaH_2 under reduced pressure at approximately 30 °C and stored over Linde 4-Å molecular sieves. The first 50 mL of distillate was discarded. Et_2O (ACS anhydrous) was distilled from Na and benzophenone. All solvents were degassed before use. Li_2Te was prepared from the stoichiometric reaction of Li and Te in liquid NH_3. $[PPh_4]_2[Pd(Te_4)_2]$,[21] $Zn(xan)_2$[27] (xan = $EtOCS_2^-$), $Cd(xan)_2$,[27] $[PPh_4]_2[MoO(Te_4)_2]$,[12] and $[PPh_4]_2[WO(Te_4)_2]$[12] were prepared by literature methods. All manipulations were carried out under N_2 with the use of standard Schlenk-line techniques or under Ar in a glove box.

Preparation of $[PPh_4]_2[Hg(Te_4)_2]$ (1). A solution of Li_2Te_4 was prepared by stirring Li_2Te (0.283 g, 2.00 mmol) and Te (0.766 g, 6.00 mmol) in DMF (15 mL) at room temperature for 2 h. To this solution was added a solution of $HgCl_2$ (0.271 g, 1.00 mmol) dissolved in DMF (5 mL), and to the resulting red-brown reaction mixture was added PPh_4Br (0.83 g, 2.0 mmol) dissolved in DMF (10 mL). The solution

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was filtered, and the filtrate was layered with Et_2O (50 mL). Red-brown crystals of $[PPh_4]_2[Hg(Te_4)_2]$ grew while the solution was stored overnight at room temperature. A second batch of product was obtained by layering additional Et_2O on the mother liquor. Total yield: 1.1 g, 60%. Anal. Calcd for $C_{48}H_{40}HgP_2Te_8$: C, 30.34; H, 2.10. Found: C, 32.0; H, 2.16. ^{125}Te NMR (DMF/CD_3CN; −30 °C): $\delta = -394$ ($J_{Hg-Te} = 3683$ Hz; $J_{Te-Te} = 1300$ Hz), 198 ($J_{Te-Te} = 1313$ Hz).

Preparation of $[PPh_4]_2[Cd(Te_4)_2]$ (2). A flask was charged with Li_2Te (0.424 g, 3.00 mmol), Te (0.766 g, 6.00 mmol), $Cd(xan)_2$ (0.355 g, 1.00 mmol), PPh_4Br (0.83 g, 2.0 mmol), DMF (30 mL), and PEt_3 (0.5 mL, 3.4 mmol). The mixture was stirred at 90 °C for 1 h and filtered. The solution was layered with Et_2O (30 mL) and stored overnight at room temperature to produce crystals of $[PPh_4]_2[Cd(Te_4)_2]$. Total yield: 0.69g, 38%. Anal. Calcd for $C_{48}H_{40}CdP_2Te_8$: C, 31.81; H, 2.21. Found: C, 31.82; H, 2.24. ^{125}Te NMR (DMF/CD_3CN: −60 °C) $\delta = -478$ ($J_{Cd-Te} = 916$ Hz), 220 ($J_{Te-Te} = 1510$ Hz).

Preparation of $[PPh_4]_2[Zn(Te_4)_2]$ (3). This compound was prepared in the same fashion as **2**, with the use of $Zn(xan)_2$ (0.308 g, 1.00 mmol) in place of $Cd(xan)_2$. Total yield: 0.62g, 35%. Anal. Calcd for $C_{48}H_{40}P_2Te_8Zn$: C, 32.65; H, 2.27. Found: C, 32.58; H, 2.25. ^{125}Te NMR (DMF/CD_3CN; −60 °C) $\delta = -337$, 224 (Possible $J_{Te-Te} = 1274$ Hz).

Crystallographic Studies. A dark red needle-shaped crystal of $[PPh_4]_2[Cd(Te_4)_2]$ was mounted in the cold stream of an Enraf-Nonius CAD4 diffractometer. Unit cell constants were determined from a least-squares analysis of the setting angles of 25 centered reflections detected between 15 and 16° in θ. Laue symmetry $4/m$ was confirmed by an analysis of the intensities of low-angle reflections. A quadrant of data ($+h,+k,\pm l$) was collected for $\theta \leq 20°$, and an octant ($+h,+k,+l$) was collected for $\theta \geq 20°$. No systematic changes were observed in the intensities of six standard reflections measured every 3 h during data collection.

The data were processed[28] and corrected for absorption[29] by methods standard in this laboratory. As the data exhibit no systematic extinctions other than those corresponding to body centering, the possible space groups are $I4$, $I\bar{4}$, and $I4/m$. Only in $I\bar{4}$ did a direct-methods solution make physical sense.[30] This solution contained two crystallographically unique Cd atoms on special positions of site symmetry $\bar{4}$, four Te atom positions corresponding to the expected structure, and a position attributable to a P atom. Refinement was complicated by the presence of disorder in the anions. There were four additional Te atom positions corresponding to an alternate ring conformation for one anion and to a second orientation, about 90° from the original orientation, for the second anion. In order to refine the structure, the Te atoms for each anion were divided into two groups corresponding to the two disordered components. This was done unambiguously by reference to known Te−Te distances. The atoms in each group were assigned a common occupancy factor, and for each anion the sum of the occupancy factors for the two groups was fixed at 1. Refinement of this model was stable, and the positions of all C atoms were revealed by difference electron density calculations following successive cycles of full-matrix least-squares calculations. Hydrogen atoms were included at calculated positions and refined with the use of a riding model. Three of the four crystallographically independent phenyl rings of the cation were found to be disordered by slight rotations around their P−C bonds. These were modeled in a manner similar to that used for the disordered Te positions. The thermal displacement parameters of corresponding C atoms were restrained to be similar. All nonhydrogen atoms were refined anisotropically. Molecular graphics for analysis of intermediate crystallographic models and for publication were produced with the SHELXTL-PC program package.[31] Selected crystallographic details are listed in Table 1, heavy-atom positions and equivalent isotropic displacement parameters are listed in Table 2, and selected bond lengths and angles are listed in Table 3. Additional crystal and experimental details, anisotropic displacement parameters, C and H atom parameters, and all bond lengths and angles are given in Tables S1−S4.[32]

Table 1. Selected Crystallographic Data for $[PPh_4]_2[M(Te_4)_2]$

chem formula	$C_{48}H_{40}P_2Te_8Zn$	$C_{48}H_{40}CdP_2Te_8$	$C_{48}H_{40}HgP_2Te_8$
T, K	108	108	108
a, (Å)	21.396(4)	21.442(3)	21.365(3)
c, (Å)	11.169(3)	11.259(2)	11.268(2)
Z	4	4	4
fw	1764.91	1811.94	1900.13
space group	$S_4^2-I\bar{4}$	$S_4^2-I\bar{4}$	$S_4^1-P\bar{4}$
density (calc), g/cm³	2.293	2.325	2.454
μ, cm⁻¹	50	49	75
$R(F)$,[a] $F_o^2 > 2\sigma(F_o^2)$	0.094	0.045	0.079
$R_w(F^2)$[b]	0.181	0.110	0.154

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F^2) = \sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2$, $w^{-1} = \sigma(F_o^2) + (0.04F_o^2)^2$ for $F_o^2 \geq 0$, $w^{-1} = \sigma(F_o^2)$ for $F_o^2 < 0$.

Table 2. Heavy-Atom Coordinates and Equivalent Isotropic Displacement Parameters (Å²) for $[PPh_4]_2[Cd(Te_4)_2]$

atom	x	y	z	U_{eq}[a]	occ
Cd(1)	1/2	0	1/4	0.0274(2)	1/4
Te(11)	0.39278(3)	−0.00706(3)	0.39421(7)	0.0330(2)	0.725(1)
Te(12)	0.44903(3)	−0.03901(3)	0.60245(7)	0.0327(2)	0.725(1)
Te(13)	0.60640(7)	−0.00597(8)	0.1033(2)	0.0277(4)	0.275(1)
Te(14)	0.55300(7)	0.03565(7)	−0.1005(2)	0.0261(4)	0.275(1)
Cd(2)	0	0	0	0.0419(3)	1/4
Te(21)	−0.02914(7)	0.10254(9)	0.1531(2)	0.0434(4)	0.566(2)
Te(22)	−0.05215(4)	0.03615(5)	0.35291(9)	0.0381(3)	0.566(2)
Te(23)	−0.05197(11)	0.09275(10)	0.1399(2)	0.0433(5)	0.434(2)
Te(24)	0.00949(6)	0.06285(5)	0.34262(12)	0.0392(4)	0.434(2)
P	0.32725(9)	0.24463(9)	0.2312(2)	0.0429(6)	1

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[PPh_4]_2[Cd(Te_4)_2]$[a]

Cd(1)−Te(11)	2.819(1)	Cd(2)−Te(21)	2.863(2)
Te(11)−Te(12)	2.724(1)	Te(21)−Te(22)	2.707(2)
Te(12)−Te(12)[a]	2.753(1)	Te(22)−Te(22)[b]	2.721(2)
Te(11)−Cd(1)−Te(11)[a]	109.65(3)	Te(21)−Cd(2)−Te(21)[b]	105.94(8)
Te(11)−Cd(1)−Te(11)[c]	109.38(2)	Te(21)−Cd(2)−Te(21)[d]	111.26(4)
Te(12)−Te(11)−Cd(1)	98.52(3)	Te(22)−Te(21)−Cd(2)	97.83(6)
Te(11)−Te(12)−Te(12)[a]	101.46(2)	Te(21)−Te(22)−Te(22)[b]	98.62(5)

[a] Symmetry transformations used to generate equivalent atoms: (a) $-x + 1, -y, z$; (b) $-x, -y, z$; (c) $y + 1/2, -x + 1/2, -z + 1/2$; (d) $y, -x, -z$.

Table 4. Heavy-Atom Coordinates and Equivalent Isotropic Displacement Parameters (Å²) for $[PPh_4]_2[Zn(Te_4)_2]$

atom	x	y	z	U_{eq}	occ
Zn(1)	0	0	1/2	0.0327(10)	1/4
Te(11)	0.10201(8)	−0.00609(8)	0.3655(2)	0.0353(5)	0.706(3)
Te(12)	0.05179(8)	−0.03833(8)	0.1511(2)	0.0335(5)	0.706(3)
Te(13)	−0.1016(2)	−0.0025(2)	0.6354(6)	0.049(2)	0.294(3)
Te(14)	−0.0525(2)	0.0359(2)	0.8476(5)	0.046(2)	0.294(3)
Zn(2)	0	1/2	1/4	0.0503(14)	1/4
Te(21)	0.0253(2)	0.5988(3)	0.1106(7)	0.0575(14)	0.505(4)
Te(22)	0.05100(13)	0.53797(14)	−0.0941(3)	0.0485(10)	0.505(4)
Te(23)	0.0523(2)	0.5869(3)	0.1163(6)	0.0520(13)	0.495(4)
Te(24)	−0.0070(2)	0.56284(13)	−0.0930(3)	0.0501(11)	0.495(4)
P	0.2554(2)	0.6727(2)	−0.0187(6)	0.047(2)	1

Data collection and structure solution for $[PPh_4]_2[Zn(Te_4)_2]$ were completely analogous to those for $[PPh_4]_2[Cd(Te_4)_2]$. The two compounds have essentially the same structures, although the disordered components have different relative occupancies. Selected crystallographic details are listed in Table 1, heavy-atom positions and equivalent isotropic displacement parameters are listed in Table 4, and selected bond lengths and angles are listed in Table 5. Additional crystal and experimental details, anisotropic displacement parameters,

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Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[PPh_4]_2[Zn(Te_4)_2]$[a]

Zn(1)–Te(11)	2.653(2)	Zn(2)–Te(21)	2.680(7)
Te(11)–Te(12)	2.714(3)	Te(21)–Te(22)	2.687(8)
Te(12)–Te(12)^{a}	2.757(3)	Te(22)–Te(22)^{b}	2.721(6)
Te(11)^{a}–Zn(1)–Te(11)	111.03(9)	Te(21)^{b}–Zn(2)–Te(21)	109.0(3)
Te(11)^{c}–Zn(1)–Te(11)	108.70(4)	Te(21)–Zn(2)–Te(21)^{d}	109.7(2)
Zn(1)–Te(11)–Te(12)	100.74(7)	Zn(2)–Te(21)–Te(22)	98.9(2)
Te(11)–Te(12)–Te(12)^{a}	99.62(6)	Te(21)–Te(22)–Te(22)^{b}	97.2(2)

[a] Symmetry transformations used to generate equivalent atoms: (a) $-x, -y, z$; (b) $-x, -y + 1, z$; (c) $y, -x, -z + 1$; (d) $y - {}^{1}/_{2}, -x + {}^{1}/_{2}, -z + {}^{1}/_{2}$.

Table 6. Heavy-Atom Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $[PPh_4]_2[Hg(Te_4)_2]$

atom	x	y	z	U_{eq}	occ
Hg(1)	0	0	0	0.0265(4)	$^1/_4$
Te(11)	−0.00849(7)	0.10661(7)	−0.1443(2)	0.0170(4)	0.801(3)
Te(12)	−0.03925(7)	0.05127(8)	−0.3524(2)	0.0166(4)	0.801(3)
Te(13)	0.0043(8)	0.1050(8)	0.140(2)	0.140(7)	0.199(3)
Te(14)	−0.0361(8)	0.0552(8)	0.351(2)	0.147(7)	0.199(3)
Hg(2)	$^1/_2$	$^1/_2$	$^1/_2$	0.0246(4)	$^1/_4$
Te(21)	0.49279(9)	0.39396(9)	0.6457(2)	0.0153(5)	0.617(3)
Te(22)	0.53486(9)	0.44631(10)	0.8504(2)	0.0153(5)	0.617(3)
Te(23)	0.5071(3)	0.3934(3)	0.3545(5)	0.060(2)	0.383(3)
Te(24)	0.5390(2)	0.4481(3)	0.1497(5)	0.056(2)	0.383(3)
Hg(3)	0	$^1/_2$	0.2221(2)	0.0350(5)	0.390(3)
Te(31)	−0.10034(14)	0.46620(13)	0.0732(2)	0.0414(7)	0.781(3)
Te(32)	−0.03356(10)	0.44609(9)	−0.1265(2)	0.0391(6)	0.781(3)
Te(33)	0.0393(10)	0.403(2)	0.369(3)	0.048(2)	0.296(5)
Te(34)	0.0541(4)	0.4675(3)	0.5711(6)	0.0383(8)	0.296(5)
Te(35)	0.0513(6)	0.4073(10)	0.367(2)	0.048(2)	0.484(3)
Te(36)	−0.0084(2)	0.4364(2)	0.5707(3)	0.0378(8)	0.484(3)
Hg(4)	0	$^1/_2$	0.2723(11)	0.091(4)	0.110(3)
Te(41)	−0.0930(7)	0.4479(7)	0.1232(12)	0.079(4)	0.219(3)
Te(42)	−0.0633(5)	0.5088(5)	−0.0869(9)	0.070(3)	0.219(3)
Te(43)	0.0278(6)	0.3950(6)	0.4099(10)	0.049(2)	0.219(3)
Te(44)	0.0518(5)	0.4573(5)	0.6099(10)	0.0388(8)	0.219(3)
P(1)	0.2412(3)	0.1760(3)	0.0171(5)	0.0277(14)	1
P(2)	0.2493(3)	0.3316(3)	0.5122(6)	0.036(2)	1

C and H atom parameters, and all bond lengths and angles are given in Tables S5–S8.[32]

$[PPh_4]_2[Hg(Te_4)_2]$ crystallizes in space group $P\bar{4}$ rather than in $I\bar{4}$. Data collection and processing were analogous to that for $[PPh_4]_2[Cd(Te_4)_2]$. Of the three unique anions in the cell, two reside on $\bar{4}$ centers and one resides on a 2-fold axis. Each of the anions on the $\bar{4}$ centers has two orientations related by a 90° rotation. The anion on the 2-fold axis (anion 3) exhibits two kinds of disorder: (1) a conformational disorder of one MTe_4 ring and (2) a second position for the entire anion related to the first by translation along the 2-fold axis. As for **2**, Te positions were assigned to particular components on the basis of known Te–Te distances. Chemically equivalent Te atoms were restrained to have similar thermal parameters. One of the cations is fully ordered, but three of the phenyl rings of the other cation are disordered. The disordered phenyl rings were each modeled as rigid groups, with corresponding C atoms in each disordered pair restrained to have similar thermal displacement parameters. The C and H atoms were refined isotropically; all others atoms were refined anisotropically. Selected crystallographic details are listed in Table 1, heavy-atom positions and equivalent isotropic displacement parameters are listed in Table 6, and selected bond lengths and angles are listed in Table 7. Additional crystal and experimental details, anisotropic displacement parameters, C and H atom parameters, and all bond lengths and angles are given in Tables S9–S12.[32]

Spectroscopy. ^{125}Te NMR spectra were obtained with the use of a Varian 400 MHz Unity Plus spectrometer equipped with a 10-mm tunable broad-band probe, a variable-temperature apparatus, and a deuterium lock. All ^{125}Te chemical shifts are referenced to an external Et_2Te standard at δ 380 ppm. Samples were made as concentrated as possible (approximately 7.5 mM) by stirring 0.1 g of crystalline product with 3 mL of a 5% CD_3CN/DMF solution and filtering the resultant mixture directly into an NMR tube.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for $[PPh_4]_2[Hg(Te_4)_2]$[a]

Hg(1)–Te(11)	2.804(2)	Hg(3)–Te(35)	2.79(2)
Te(11)–Te(12)	2.707(3)	Hg(3)–Te(31)	2.816(3)
Te(12)–Te(12)^{a}	2.759(3)	Te(31)–Te(32)	2.699(4)
Hg(2)–Te(21)	2.802(2)	Te(32)–Te(32)^{c}	2.713(4)
Te(21)–Te(22)	2.716(3)	Te(35)–Te(36)	2.70(2)
Te(22)–Te(22)^{b}	2.735(4)	Te(36)–Te(36)^{c}	2.742(7)
Te(11)^{a}–Hg(1)–Te(11)	109.12(7)	Te(35)–Hg(3)–Te(35)^{c}	108.5(9)
Te(11)^{d}–Hg(1)–Te(11)	109.65(4)	Te(35)–Hg(3)–Te(31)	117.7(4)
Te(12)–Te(11)–Hg(1)	99.40(6)	Te(35)^{c}–Hg(3)–Te(31)	103.3(3)
Te(11)–Te(12)–Te(12)^{a}	101.49(6)	Te(31)–Hg(3)–Te(31)^{c}	106.89(13)
Te(21)^{b}–Hg(2)–Te(21)	108.27(9)	Te(32)–Te(31)–Hg(3)	97.75(11)
Te(21)^{e}–Hg(2)–Te(21)	110.07(4)	Te(31)–Te(32)–Te(32)^{c}	98.29(9)
Te(22)–Te(21)–Hg(2)	98.42(8)	Te(36)–Te(35)–Hg(3)	98.5(6)
Te(21)–Te(22)–Te(22)^{b}	99.50(8)	Te(35)–Te(36)–Te(36)^{c}	99.6(4)

[a] Symmetry transformations used to generate equivalent atoms: (a) $-x, -y, z$; (b) $-x + 1, -y + 1, z$; (c) $-x, -y + 1, z$; (d) $y, -x, -z$; (e) $-y + 1, x, -z + 1$.

Results and Discussion

Synthesis. $[PPh_4]_2[Zn(Te_4)_2]$ and $[PPh_4]_2[Cd(Te_4)_2]$ can be made by reacting the metal xanthates with a polytelluride solution in DMF at 90 °C, followed by the addition of PPh_4Br:

$$M(S_2COEt)_2 + 2Te_4^{2-} + PPh_4^{+} \rightarrow [PPh_4]_2[M(Te_4)_2] + 2S_2COEt^{-} \quad (1)$$

$$M = Zn, Cd$$

The yield can be improved through the addition of a small amount of PEt_3. Its role is uncertain, but we believe the PEt_3 provides an anhydrous environment and basic condition and also prevents the deposition of elemental Te by forming soluble $TePEt_3$.

When the analogous reaction is carried out with $Hg(xan)_2$, crystals of $[PPh_4]_2[Hg(Te_4)_2]$ and $[PPh_4]_2[HgTe_7]$[8] are isolated. When the reaction is carried out with $HgCl_2$ in place of $Hg(xan)_2$, higher yields of the compounds are obtained. X-ray powder diffraction confirms the presence of both $[PPh_4]_2[Hg(Te_4)_2]$ and $[PPh_4]_2[HgTe_7]$; however ^{125}Te NMR spectra of the redissolved crystals show only resonances attributable to $[Hg(Te_4)_2]^{2-}$. The $[HgTe_7]^{2-}$ and $[ZnTe_7]^{2-}$ anions have been isolated from the reaction of $M(OAc)_2$ with potassium polytelluride in the presence of 15-crown-5.[9] However, we see no evidence of impurities in our $[PPh_4]_2[Zn(Te_4)_2]$ samples.

When Ni and Pt xanthates are reacted according to eq 1, only the cubanes $[PPh_4]_4[Ni_4Te_4(Te_2)_2(Te_3)_4]$[33] and $[PPh_4]_4[Pt_4Te_4(Te_3)_6]$[34] are isolated. Attempts to synthesize the $[Ni(Te_4)_2]^{2-}$ anion by reaction of $[Ni(Se_4)_2]^{2-}$ with $TePEt_3$ were reported earlier; these also yield the $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$ anion.[34]

Crystal Structures. The crystal structures of $[PPh_4]_2[M(Te_4)_2]$, M = Hg, Cd, Zn, are surprisingly complex. The three structures each consist of $[M(Te_4)_2]^{2-}$ anions packed in channels along the lines $0,0,z$; $0,{}^1/_2,z$; and ${}^1/_2,{}^1/_2,z$ among the phenyl groups of the $[PPh_4]^+$ cations. Parts of two of these channels are contained in the asymmetric units of the body-centered structures (M = Zn, Cd), while parts of three channels are contained in the asymmetric unit of the primitive Hg structure. Each unit cell contains exactly one anion in each channel; hence the length of the *c* axis corresponds to the length of one anion, including a van der Waals spacing on each end. In the $[PPh_4]_2[Hg(Te_4)_2]$ structure, the anion on the 2-fold axis

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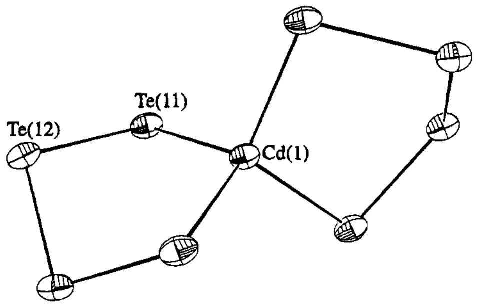

Figure 1. View of the principal component of one disordered $[Cd(Te_4)_2]^{2-}$ anion, with the 50% probability thermal ellipsoids shown. The anion possesses crystallographically imposed $\bar{4}$ symmetry.

is disordered on either side of 0,$^1/_2$,$^1/_4$; if the anion were not disordered but rather its Hg atom were positioned exactly at 0,$^1/_2$,$^1/_4$, then the Zn, Cd, and Hg structures would be the same. Since the cation packing is similar in all three structures, we attribute the orientational disorder among the anions to the fact that the channels in which they reside are essentially square, providing little energetic difference between the two orientations. To avoid vacancies and close Te−Te contacts, all of the anions in a particular channel must adopt the same orientation. Then the nearest intermolecular Te−Te contacts in these structures are all greater than 3.83 Å. There are no direct contacts between anions in different channels, and we presume that the orientation of the anions in a given channel is independent of the orientations of the anions in other channels. This is consistent with the fact that the ratios of the orientationally disordered components vary from about 80:20 to near 60:40 and that these ratios differ for different unique anions in the Hg structure.

The structures of the anions themselves are as expected, consisting of metal atoms tetrahedrally coordinated by two Te_4^{2-} bidentate ligands (Figure 1). Except in one disordered pair of anions that reside on a 2-fold axis in the $[PPh_4]_2[Hg(Te_4)_2]$ structure, all of the metal atoms reside on sites of symmetry $\bar{4}$. All of the MTe_4 rings are constrained by symmetry to have 2-fold symmetry and therefore have the half-chair conformation.[16]

Owing to the extensive disorder in these structures, metrical details must be treated with caution. In particular, it is very likely that the standard deviations derived from the least-squares process are severely underestimated. Thus the cations in the structures of **1**−**3** show some apparent distortions, with P−C distances ranging from 1.62(5) to 2.00(3) Å, C−C distances ranging from 1.12(5) to 1.59(4) Å, and angles about the C atoms ranging from 105(4) to 129(2)°. Metrical data for the heavy atoms are more reliable, and they show a good degree of internal consistency. The M−Te and Te−Te bond lengths in the major components of these structures appear normal. The Zn−Te distances of 2.653(2) and 2.680(7) Å in $[PPh_4]_2[Zn(Te_4)_2]$ are somewhat longer than the distances of 2.542(5) and 2.518(3) Å in the extensively disordered structure of $[K(15\text{-crown-}5)_2]_2[ZnTe_7]$,[9] the only other tellurozincate known. However, the latter Zn−Te distances are surprisingly short, hardly longer than the Zn−Se distances of 2.450(5)−2.493(6) Å in $[PPh_4]_2[Zn(Se_4)_2]$.[20] The Cd−Te distances of 2.819(1) and 2.863(2) in $[PPh_4]_2[Cd(Te_4)_2]$ are comparable to distances of 2.733(2)−2.935(2) Å in $[Na(15\text{-crown-}4)]_4[Cd_4Te_{12}]\cdot 8DMF$.[35] The Hg−Te distances of 2.804(2), 2.802(2), 2.79(2), and 2.816(3) Å in $[PPh_4]_2[Hg(Te_4)_2]$ are comparable to distances of 2.706−2.983 Å in $[N(n\text{-}Bu)_4]_4[Hg_4Te_{12}]$,[36] to distances averaging 2.71 Å in $[PPh_4]_{2n}[HgTe_5]_n$,[36] and to distances of 2.722(2)−2.742(1) Å in $[PPh_4]_2[HgTe_7]$.[8] The Te−Te distances are similar in the three present structures, ranging from 2.687(8)−2.759(2) Å. These may be compared to separations of 2.684(4)−3.253(3) Å in the above compounds.[8,9,35,36] The angles about the metal centers in the present structures range from 103.3(3) to 117.7(4)°, and the angles around Te atoms range from 97.2(2) to 101.49(6)°.

Table 8. ^{125}Te NMR Resonances in Some Tellurometalates

anion[a]	temp, °C	metal-bound	ring-bound
$[MoO(Te_4)_2]^{2-\,b}$	20	801	−5
$[MoO(Te_4)_2]^{2-}$	20	814 (7638[c])	7
$[WO(Te_4)_2]^{2-\,b}$	20	597	−191
$[WO(Te_4)_2]^{2-}$	20	607 (315[d])	−181
$[Pd(Te_4)_2]^{2-}$	20	823	616
$[Zn(Te_4)_2]^{2-}$	−60	−337	224 (1274[h])
$[Cd(Te_4)_2]^{2-}$	−60	−478 (916[e])	220 (1510[g])
$[Hg(Te_4)_2]^{2-}$	−30	−394 (3683,[f] 1300[g])	198 (1313[g])

[a] From PPh_4^+ salts. [b] From ref 12. [c] J_{Mo-Te}, Hz. [d] J_{W-Te}, Hz. [e] Average J_{Cd-Te}, Hz, for ^{111}Cd and ^{113}Cd. [f] J_{Hg-Te}, Hz. [g] J_{Te-Te}, Hz. [h] Possible J_{Te-Te}, Hz.

Spectroscopy. The ^{125}Te chemical shifts and coupling constants for the $[M(Te_4)_2]^{2-}$ and $[MO(Te_4)_2]^{2-}$ anions are listed in Table 8. As in the analogous selenometalates, two resonances appear in the ^{125}Te NMR spectra, one assignable to the four metal-bound Te centers and one assignable to the four ring-bound Te centers. Within the Zn triad, both Cd and Hg have spin $^1/_2$ isotopes (^{111}Cd, 12.26%; ^{113}Cd, 12.75%; ^{199}Hg, 16.84%). Satellite resonances arising from M−Te coupling allow assignment of the upfield resonance to the metal-bound Te nuclei for both the $[Hg(Te_4)_2]^{2-}$ and $[Cd(Te_4)_2]^{2-}$ anions. The resonances in the spectrum of the $[Zn(Te_4)_2]^{2-}$ anion are assigned by analogy to those in the spectra of the Cd and Hg complexes. In the Ni triad, only Pt has an NMR-active nucleus (^{195}Pt, spin $^1/_2$, 33.8%). As the $[Pt(Te_4)_2]^{2-}$ anion is unknown, assignments of the ^{125}Te resonances of the $[Pd(Te_4)_2]^{2-}$ anion cannot be made by analogy, but only by reference to the assignments in the corresponding selenometalates, where it is the downfield resonance that arises from the metal-bound Se nuclei.

The ^{125}Te NMR spectra of the $[M(Te_4)_2]^{2-}$ anions are most easily observed in the order Hg, Cd, Zn. Thus at 25 °C the spectrum of the $[Hg(Te_4)_2]^{2-}$ anion was observed, along with satellites about the metal-bound Te center arising from Hg−Te coupling . When the sample was cooled to −30 °C, the signal-to-noise improved, and satellites around each peak arising from Te−Te coupling were observed. No satellites from Cd−Te coupling were observed in the spectrum of the $[Cd(Te_4)_2]^{2-}$ anion until the sample was cooled to −30 °C, and only at −60 °C were satellites arising from Te−Te coupling observed about the downfield peak. No satellites were resolved about the rather broad upfield peak (metal-bound Te). Broadening presumably arises from the contributions of both ^{111}Cd and ^{113}Cd nuclei, which have similar gyromagnetic ratios and natural abundances. No spectrum could be observed for the $[Zn(Te_4)_2]^{2-}$ anion at 25 °C. Two broad resonances were observed at 0 °C; at −60 °C these peaks narrowed and possible Te−Te coupling was observed on the ring-bound Te. Owing to the freezing of the DMF solvent, spectra were not obtained at temperatures lower than −60 °C. An alternative solvent could not be found.

The ^{125}Te spectra of the $[MO(Te_4)_2]^{2-}$ anions (M = W, Mo) were discussed previously,[12] but for the W compound no coupling to ^{183}W (spin $^1/_2$, 14.3%) was reported. We observe satellite resonances arising from coupling of the metal-bound Te to ^{183}W and ^{95}Mo at the downfield resonance for these W(IV) and Mo(IV) (d^2) systems.

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The resulting trends in the ^{125}Te and ^{77}Se chemical shifts are similar. For the analogous selenometalates the peak-order inversion and large differences in chemical shifts between the Ni and Zn triads have been discussed previously in terms of the differing abilities of d^8 and d^{10} metals to accept electron density from the ligands.[20]

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Supplementary Material Available: Experimental details (Tables S1, S5, and S9), anisotropic displacement parameters (Tables S2, S6, and S10), C and H atom parameters (Tables S3, S7, and S11), and bond lengths and angles (Tables S4, S8, and S12) for **1**–**3** (43 pages). Ordering information is given on any current masthead page.

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