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Synthesis and Structure of $[PPh_4]_3[Cr(Te_4)_3]\cdot DMF$: The First Tris(tetratelluride) Complex

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The compound $[PPh_4]_3[Cr(Te_4)_3]\cdot DMF$ has been synthesized from the reaction of $Cr(CO)_6$ with a polytelluride solution in dimethylformamide at 100 °C. The compound has been characterized by ^{125}Te NMR and single-crystal X-ray diffraction techniques. The compound crystallizes in the triclinic space group $P\bar{1}$, with $a = 12.991(3)$ Å, $b = 14.782(3)$ Å, $c = 24.628(5)$ Å, $\alpha = 90.63(3)°$, $\beta = 104.45(3)°$, $\gamma = 106.49(3)°$, and $Z = 2$ ($T = 153$ K). The $[Cr(Te_4)_3]^{3-}$ anion consists of a Cr(III) center chelated by three Te_4^{2-} ligands in a distorted octahedral environment. The anion has the $\Delta\lambda\lambda\lambda$ (or $\Lambda\delta\delta\delta$) conformation.

The chemistry of tellurometalates continues to expand rapidly,[1−23] and many new compounds have been reported that have no sulfur or selenium analogues. Several tellurometalates contain mono- or bis(tetratelluride) ligands, including $[Cr(CO)_4(Te_4)]^{2-}$,[18] $[M(Te_4)_2]^{2-}$ (M = Zn, Cd, Hg, Pd),[19,20] $[O{=}M(Te_4)_2]^{2-}$ (M = W, Mo),[21] $[M_2(\mu\text{-}Te_4)(Te_4)_2]^{4-}$ (M = Cu, Ag),[1,8] and $[Cr_3(Te_4)_6]^{3-}$.[23] However, structurally characterized octahedral chalcogeno metalates of the type $[M(Q_4)_3]^{n-}$ (Q = S, Se) are limited and none are known for Q = Te. Examples include $[Pt(Se_4)_3]^{2-}$,[24,25] $[Ir(Se_4)_3]^{3-}$,[26,27] $[Sn(S_4)_3]^{2-}$,[28] and $[Sn(Se_4)_3]^{2-}$.[29,30] Here, we report the first tellurometalate containing tris(tetratelluride) ligands, namely, $[PPh_4]_3[Cr(Te_4)_3]\cdot DMF$.

$[PPh_4]_3[Cr(Te_4)_3]\cdot DMF$ was synthesized from the reaction of $Cr(CO)_6$ with 3 equiv of polytelluride anions in DMF at 100 °C, followed by the addition of PPh_4Br and THF.[31] Attempts to synthesize the W and Mo analogues by this same route were unsuccessful. Note that $[PPh_4]_2[Cr(CO)_4(Te_4)]$ was previously synthesized under similar conditions from the reaction of equimolar amounts of $Cr(CO)_6$ and K_2Te_4 in

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[31] K_2Te_3 (922 mg, 2.0 mmol), Te (256 mg, 2.0 mmol), and $Cr(CO)_6$ (150 mg, 0.68 mmol) were dissolved in DMF (20 mL) in a 100 mL Schlenk flask. The reaction mixture was stirred overnight at 100 °C and then cooled to room temperature. The resulting red-brown solution was treated with a solution of PPh_4Br (838 mg, 2.0 mmol) dissolved in DMF (10 mL), and then THF (20 mL) was added. The resultant mixture was filtered, and the filtrate was layered with THF (20 mL). Black air-sensitive crystals of $[PPh_4]_3[Cr(Te_4)_3]\cdot DMF$ suitable for X-ray diffraction studies formed after several weeks at 5 °C in 28% yield. Anal. Calcd for $C_{72}H_{60}CrP_3Te_{12}\cdot DMF$: C, 33.7; H, 2.53; N, 0.52. Found: C, 33.9; H, 2.44; N, 0.60. ^{125}Te NMR (DMF): $\delta = -649$, 352 (external standard Ph_2Te_2 at δ 422 ppm).

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DMF.[18] $[PPh_4]_3[Cr_3(Te_4)_6]$ was also previously synthesized from the reaction of K_2Te_2 with $CrCl_3$ in DMF.[23] Before the present results, only these two examples of compounds containing polytelluride rings chelated to chromium centers were known. The reaction of a 3-fold excess of $Cr(CO)_6$ with various polytellurides (K_2Te, K_2Te_2, K_2Te_3, and $(PPh_4)_2(Te_4)$) in DMF leads to the formation of the unusual metal-rich products, $[Cr_4(CO)_{18}(\mu_3\text{-}Te)_2]^{2-}$,[32] $[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_2)]^{2-}$,[32] and $[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_3)]^{2-}$.[32] Their structures contain either a Cr_2Te_2 ring with a transannular Cr−Cr bond or Te_n^{2-} ($n = 2, 3$) chains with two $Cr(CO)_5$ fragments bound to lone pairs on each terminal Te ligand. Moreover, the reaction of a 1:1 ratio of $Cr(CO)_6$ and K_2Te_4 in ethylenediamine (en) in the presence of 2,2,2-cryptand yields $[Cr(CO)_5(\eta^1\text{-}Te_3)]^{2-}$,[33] whereas a 4:1 ratio affords $[(Cr(CO)_5)_2(\mu\text{-}Te_2)]^{2-}$.[33] Once again this illustrates that the formation of tellurometalates depends critically on the tellurium source, the stoichiometry of the reactants, the choice of solvent, and the reaction conditions.

The crystal structure of $[PPh_4]_3[Cr(Te_4)_3]\cdot DMF$ consists of well-separated cations and anions.[34] The $[Cr(Te_4)_3]^{3-}$ anion consists of a Cr(III) center chelated by three Te_4^{2-} ligands in a distorted octahedral environment. The anion $[Cr(Te_4)_3]^{3-}$ has neither a sulfur nor a selenium analogue; in fact, it is the first example of a compound containing three Te_4^{2-} rings coordinated to a metal center. The molecule in Figure 1 has the $\Delta\lambda\lambda\lambda$ conformation. Conformations for the known $M(Q_4)_3{}^{n-}$ anions are tabulated in Table 1. Since all of these compounds crystallize in centrosymmetric space groups, each anion has a corresponding enantiomer of the Λ conformation. From earlier studies of $[M(en)_3]^{n+}$ systems (M = Cr(III),[35] Ru(II),[36] Co(III),[37] Rh(III)[38]), the relative stabilities of the various conformers in solution were established to be $\Delta\lambda\lambda\delta > \Delta\lambda\lambda\lambda \approx \Delta\lambda\delta\delta > \Delta\delta\delta\delta$.[39] Not surprisingly, the stabilities established for the $[M(en)_3]^{n+}$ systems do not apply to the $[M(Q_4)_3]^{n-}$ systems.

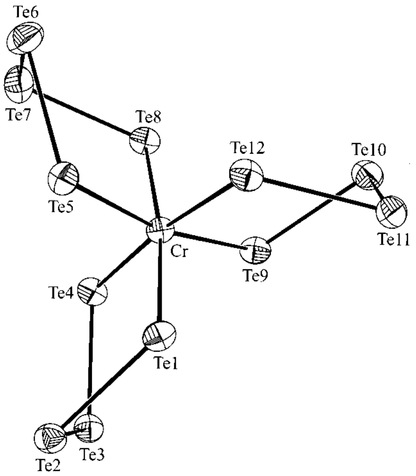

Figure 1. Structure of the $[Cr(Te_4)_3]^{3-}$ anion. The Δ enantiomer is shown. Displacement ellipsoids are shown at the 50% probability level. The Cr−Te bond distances range from 2.702(1) to 2.719(1) Å, and the Te−Te distances range from 2.707(10) to 2.826(12) Å. The Te−Cr−Te angles within the Te_4 rings are 100.32(4)°, 100.83(4)°, and 98.84(4)°.

Table 1. Conformations for the Known $M(Q_4)_3{}^{n-}$ Anions[a]

compound	conformation	ref
$[Pt(Se_4)_3]^{2-}$, α form (dilute solution, +25 °C)	$\Delta\lambda\lambda\delta$	25
$[Pt(Se_4)_3]^{2-}$, β form (concd solution, −40 °C)	$\Delta\lambda\delta\delta$	25
$[Ir(Se_4)_3]^{3-}$ (K(18-crown-6) salt)	$\Delta\lambda\lambda\lambda$	26, 27
$[Ir(Se_4)_3]^{3-}$ (K(2.2.2-cryptand) salt)	$\Delta\lambda\lambda\delta$	27
$[Sn(S_4)_3]^{2-}$	$\Delta\lambda\delta\delta$	28
$[Sn(Se_4)_3]^{2-}$	$\Delta\lambda\delta\delta$	29, 30
$[Cr(Te_4)_3]^{3-}$	$\Delta\lambda\lambda\lambda$	*b*

[a] Each anion has a corresponding enantiomer of the Λ conformation. [b] This work.

The ^{125}Te NMR spectrum of a DMF solution of $[PPh_4]_3[Cr(Te_4)_3]$ at room temperature shows two resonances at δ −649 and 352 ppm. The resonance at δ −649 ppm is assigned to the Te nucleus bound to Cr, and the second resonance at δ 352 ppm is attributed to the ring Te. Previous NMR studies on Cr(III) compounds indicate that ^1H, ^{13}C, ^{31}P, and ^{14}N resonances are slightly shifted from the resonances of the free ligands.[40,41] We thus assume that this is also true for ^{125}Te resonances. The values found here may be compared with those of −337,224; −478,220; and −394,-198 in $[M(Te_4)_2]^{2-}$, M = Zn, Cd, Hg.[19]

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Supporting Information Available: Crystallographic data in CIF format for $[PPh_4]_3[Cr(Te_4)_3]\cdot DMF$. This material is available free of charge via the Internet at http://pubs.acs.org.

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