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Heteroatomic Polyanions of Post Transition Metals. Synthesis and Crystal Structure of a Salt of Ditelluromercurate(II), $HgTe_2^{2-}$

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As part of a continuing study of the preparation and structures of homo- and heteropolyatomic anions of the heavier post transition elements we recently reported the structure of the $Tl_2Te_2^{2-}$ anion.[2] This species was prepared by the room-temperature reaction of the ternary alloy composition KTlTe with 2,2,2-crypt in ethylenediamine (en). Subsequently, we have examined the reactions of the alloy composition KHgX, where X = Sn, Sb, or Te, under the same conditions. These studies have shown that heteropolyatomic anions containing mercury form with Sn and Te but not with Sb under the same experimental conditions. We report here the preparation and X-ray crystal structure of $(2,2,2\text{-crypt-K}^+)_2HgTe_2^{2-}\cdot$en, which contains the linear $HgTe_2^{2-}$ anion, the first species of this type to be isolated for mercury.

Experimental Section

Synthesis of $(2,2,2\text{-crypt-K}^+)_2HgTe_2^{2-}\cdot$en. A 0.098-g (0.266-mmol) quantity of the alloy composition KHgTe (prepared by reacting stoichiometric amounts of KHg[3] and Te (99.999%, United Mineral and Chemical Co.) at 600 °C in a sealed tantalum tube for 12 h followed by quenching to room temperature) was allowed to react with 0.100 g (0.266 mmol) of 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) (Merck) in ca. 8 cm^3 of dry ethylenediamine (en). This initially gave a red solution around the alloy, which on gentle shaking or diffusion quickly produced a yellow solution. There was also evidence for an additional blue intermediate. The red and blue colors could be indicative of the initial formation of Te_3^{2-} and Te_2^{2-}, respectively,[4] which subsequently react with the alloy to give $HgTe_2^{2-}$. After ca. 3 days the red color ceased to form around the alloy, and the solution was intensely yellow. Slow evaporation of the en from the decanted solution gave large, block-shaped yellow crystals, which were washed with ethylamine to remove any excess crypt. After being cut to an appropriate size suitable specimens were selected for X-ray diffraction by oscillation photographs. The crystals instantly turn black on exposure to moist air and so were sealed in 0.3-mm o.d. capillaries.

X-ray Data Collection and Processing of Data. An approximately block-shaped crystal of dimensions 0.32 × 0.24 × 0.18 mm was examined on a four-circle automated diffractometer built in Ames Laboratory and described elsewhere,[5] using graphite monochromated Mo Kα radiation (λ = 0.710 34 Å). The initial orientation procedure indicated triclinic symmetry, and data were collected to $2\theta \leq 50°$ for the octants HKL, $\bar{H}\bar{K}L$, $\bar{H}KL$, and $H\bar{K}\bar{L}$ at ca. 24 °C. The intensities of three standards ($26.2° < 2\theta < 33.4°$) were measured after every 75 reflections to check on crystal alignment and decay; these showed no significant change in intensity over the period of data collection. A total of 5594 reflections (excluding standards) were measured. An empirical absorption correction (μ = 42.06 cm^{-1}) using a ϕ-scan method[5] (ϕ = 0–350° with $\Delta\phi$ = 10°) at θ = 17.24° was applied to the data. Transmission factors ranged from 0.77 to 0.99. After accounting for Lorentz and polarization effects and absorption, we obtained a final data set of 4400 reflections after averaging in $P\bar{1}$ ($R(I)$ = 1.65% for 748 duplicate reflections) with $I > 3\sigma(I)$ and $F > 3\sigma(F)$.

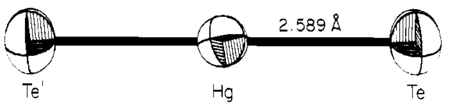

Figure 1. Perspective view of the $HgTe_2^{2-}$ anion in $(2,2,2\text{-crypt-K}^+)_2HgTe_2^{2-}\cdot$en. A crystallographic center of inversion occurs at Hg. Thermal ellipsoids are shown at the 50% probability level.

Precise unit cell dimensions were obtained on the same crystal by a least-squares fit to the 2θ values of 23 reflections in the range $27° < 2\theta < 35°$, which were turned on both Friedel-related peaks to avoid centering and instrument errors. The results were a = 11.263 (1) Å, b = 12.171 (2) Å, c = 10.335 (2) Å, α = 107.00 (2)°, β = 91.18 (2)°, γ = 88.36 (2)°, and V = 1352.2 (3) Å^3.

Solution and Refinement of the Structure. A preliminary Howells–Phillips–Rogers statistical test was inconclusive as to the choice of space group ($P\bar{1}$ or $P1$), so the structure was initially refined by assuming the centric space group $P\bar{1}$. Solution of the structure was achieved by inspection of the Patterson map, from which the heavy-atom positions were easily obtained. The remaining nonhydrogen atoms (in both crypt and en) were subsequently located from Fourier maps. Full-matrix least-squares refinement of all positional and either anisotropic (Hg, Te, K, O, N) or isotropic (C and en atoms) thermal parameters including a reweight in 50 groups (to correct for a dependence of $\sum w(|F_o| - |F_c|)^2$ on F_o) led to convergence (maximum $\Delta/\sigma \leq 0.10$) with R = 0.049 and R_w $(=[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2})$ = 0.065.

The standard deviations and thermal ellipsoids for the light atoms at this stage were very satisfactory and gave no hint that an acentric ordering pertained. The tellurium atom thermal parameters gave only a *very slight* suggestion of bending (or libration) of the anion (see below). However, an analogous refinement of 61 nonhydrogen atoms after tellurium displacement using a data set averaged in $P1$ (5099 reflections with $R(I)$ = 1.53% for 49 duplicate reflections) showed no improvement in the residuals, and the heavy-atom positions were within 3σ of those obtained in $P\bar{1}$. Furthermore, comparison of the distances between the light atoms (N–C, O–C, C–C) indicated that the spread around the average values was considerably larger in the case of the acentric space group. We therefore conclude that the correct choice of space group is $P\bar{1}$. A final difference Fourier map was flat to ±0.5 e Å^{-3} throughout.

Sources of the programs, procedures, and neutral-atom scattering data (including corrections for the real and imaginary parts of anomalous dispersion) were as previously reported.[2]

Results and Discussion

The crystal data plus final atomic positional and thermal parameters for the 31 nonhydrogen atoms in $(2,2,2\text{-crypt-K}^+)_2HgTe_2^{2-}\cdot$en are given in Table I. Important distances and angles are discussed below; distances and angles in the 2,2,2-crypt-K$^+$ cations and en molecule and a listing of the observed and calculated structure factors are given in the supplementary material (Tables II, III). A view of the $HgTe_2^{2-}$ anion is shown in Figure 1.

The compound consists of 2,2,2-crypt-K$^+$ cations, $HgTe_2^{2-}$ anions, and en molecules. The mercury atoms sit on the inversion center at the origin while the en molecules are centered about the inversion center at 0, $^1/_2$, 0. There is, accordingly, a stacking of alternate anions and en molecules along y. All anion–cation and anion–en distances are larger than 3.69 Å (neglecting undetermined hydrogen atom positions), suggesting little interaction between ions (and with en) in this structure. Those distances less than 4.0 Å to $HgTe_2^{2-}$ are C(9), 3.69 (1) Å, and C(2), 3.97 (1) Å, to Hg and C(15), 3.85 (1) Å, and N(en), 3.94 (2) Å, to Te.

The conformations of the 2,2,2-crypt-K$^+$ cations are similar to those in other symmetry-unconstrained cations found in $(2,2,2\text{-crypt-K}^+)_2Tl_2Te_2^{2-}\cdot$en[2] and $(2,2,2\text{-crypt-K}^+)_2Te_3^{2-}\cdot$en,[4] and all are, in turn, similar to that found in $2,2,2\text{-crypt-K}^+)I^-$.[7]

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(1) Operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Materials Sciences Division.

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Table I. Crystal Data and Atomic Parameters for $(2,2,2\text{-crypt-K}^+)_2HgTe_2{}^{2-}\cdot en$

monoclinic, $P\bar{1}$; $a = 11.263$ (1) Å, $b = 12.171$ (2) Å, $c = 10.335$ (2) Å, $\alpha = 107.00$ (2)°,
$\beta = 91.18$ (2)°, $\gamma = 88.36$ (2)°; $V = 1352.2$ (3) Å^3, $Z = 1$, fw = 1347.09, $\rho_{calcd} = 1.65$ g/cm^3

atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg	0.0	0.0	0.0	7.50 (3)	7.16 (3)	9.93 (5)	−0.14 (2)	−0.10 (3)	2.03 (3)
Te	0.15181 (5)	0.16038 (5)	0.09552 (6)	10.73 (6)	9.28 (5)	15.78 (8)	−2.85 (4)	−0.27 (5)	1.70 (5)
K	0.6173 (1)	0.2693 (1)	0.6033 (1)	6.3 (1)	6.6 (1)	9.1 (1)	−0.3 (1)	0.1 (1)	1.8 (1)
N(1)	0.8540 (6)	0.2251 (6)	0.4741 (8)	7.7 (5)	11.8 (7)	17.8 (10)	0.0 (5)	2.4 (6)	2.5 (6)
N(2)	0.3780 (5)	0.3160 (6)	0.7320 (6)	8.4 (5)	10.3 (6)	12.7 (7)	0.0 (4)	2.6 (5)	2.4 (5)
O(1)	0.6392 (5)	0.1013 (5)	0.3458 (5)	11.1 (5)	11.8 (5)	10.4 (6)	0.7 (4)	1.3 (4)	1.2 (4)
O(2)	0.4143 (4)	0.1802 (4)	0.4526 (5)	8.5 (4)	8.5 (4)	15.1 (7)	−1.8 (3)	−2.0 (4)	0.2 (4)
O(3)	0.8108 (5)	0.2118 (5)	0.7430 (7)	10.8 (5)	12.7 (6)	19.1 (9)	1.2 (4)	−3.0 (5)	6.6 (6)
O(4)	0.5776 (5)	0.2079 (5)	0.8403 (5)	12.7 (6)	12.5 (5)	11.0 (6)	−0.6 (4)	−1.6 (5)	3.9 (5)
O(5)	0.7399 (5)	0.4542 (4)	0.5584 (6)	9.5 (5)	8.2 (4)	16.4 (7)	−2.8 (3)	1.4 (5)	1.1 (4)
O(6)	0.5417 (5)	0.4998 (4)	0.7343 (6)	12.3 (5)	7.5 (4)	15.3 (7)	0.7 (4)	0.6 (5)	3.5 (4)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(1)	0.850 (1)	0.114 (1)	0.366 (1)	7.0 (2)	C(11)	0.469 (1)	0.248 (1)	0.915 (1)	6.5 (2)
C(2)	0.745 (1)	0.101 (1)	0.272 (1)	7.1 (2)	C(12)	0.367 (1)	0.241 (1)	0.818 (1)	6.2 (2)
C(3)	0.536 (1)	0.092 (1)	0.263 (1)	6.5 (2)	C(13)	0.877 (1)	0.319 (1)	0.418 (1)	7.0 (2)
C(4)	0.428 (1)	0.076 (1)	0.341 (1)	6.3 (2)	C(14)	0.862 (1)	0.438 (1)	0.519 (1)	7.0 (2)
C(5)	0.305 (1)	0.178 (1)	0.518 (1)	6.4 (2)	C(15)	0.727 (1)	0.556 (1)	0.670 (1)	6.5 (2)
C(6)	0.286 (1)	0.291 (1)	0.625 (1)	6.1 (2)	C(16)	0.600 (1)	0.588 (1)	0.690 (1)	6.3 (2)
C(7)	0.946 (1)	0.216 (1)	0.574 (1)	7.5 (2)	C(17)	0.417 (1)	0.520 (1)	0.745 (1)	5.8 (2)
C(8)	0.910 (1)	0.152 (1)	0.669 (1)	7.4 (2)	C(18)	0.365 (1)	0.441 (1)	0.812 (1)	6.1 (2)
C(9)	0.784 (1)	0.167 (1)	0.855 (1)	7.1 (2)	N(en)	0.954 (1)	0.440 (1)	0.135 (2)	14.8 (5)
C(10)	0.679 (1)	0.229 (1)	0.928 (1)	7.0 (2)	C(en)	0.977 (4)	0.527 (3)	0.047 (4)	22.0 (12)

[a] Thermal parameters ($\times 10^3$) of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ are listed.

The K–N distances are 2.970 (7) and 2.996 (6) Å, and the K–O distances vary from 2.774 (6) to 2.853 (6) Å. There is a possible shift (0.026 Å, 2.8σ) of the potassium atom toward the end of the crypt ligand associated to a greater extent with the anion and en molecule. Similar effects have been observed in the structures of the 2,2,2-crypt–potassium salts of $Te_3{}^{2-}$ (0.09 Å, 2.3σ) and $Bi_4{}^{2-}$ (0.09 Å, 3σ).[2,8] We also note some small but significant differences among the K–O distances.

The $HgTe_2{}^{2-}$ anion, which must be linear by virtue of the inversion center, has a Hg–Te bond length of 2.5890 (8) Å. This may be compared with a calculated value of 2.65 Å based on covalent radii for digonal mercury (1.30 Å)[9] and tellurium (1.35 Å).[10] A slightly closer value (2.63 Å) may be obtained by using a covalent radius for mercury calculated from the Hg–Hg distances in $Hg_3(AsF_6)_2$ and $Hg_3(AlCl_4)_2$.[11,12] In either case the observed distance appears significantly smaller than calculated. Comparison with the Hg–Te distance (2.78 Å)[13] in HgTe, which has the zinc-blende (sphalerite) structure, is not appropriate here as both atoms are tetrahedrally bonded in this material.

The $HgTe_2{}^{2-}$ anion has an analogue with the lighter group 6 element oxygen in $HgO_2{}^{2-}$, which has been structurally characterized in the compounds Na_2HgO_2 and K_2HgO_2.[14] In both, the $HgO_2{}^{2-}$ group is linear, and the Hg–O distances are 1.96 Å (×2) and 1.93 Å (×2), respectively. Here we note that the Hg–O distance is significantly less than the sum of the covalent radii for the respective elements (2.03 Å), as is also observed for $HgTe_2{}^{2-}$. For cinnabar, HgS, there are helical chains in which the Hg has two nearest sulfur neighbors at 2.36 Å, two more at 3.10 Å, and two more at 3.30 Å, with a S–Hg–S bond angle of 172°.[15] In this case the Hg–S distance appears greater than the sum of the respective covalent radii (2.32 Å), presumably as a result of the extra Hg–S contacts, which reduce the bond order within the chain and increase the directly bonded Hg–S distance. Work on the mercury–tin system is continuing.

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Registry No. $(2,2,2\text{-crypt-K}^+)_2HgTe_2{}^{2-}$, 79172-66-0; KHgTe, 79172-67-1.

Supplementary Material Available: Listings of bond distances and angles in the cations and en and structure factor amplitudes, Tables II and III (14 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Trichloro[1,3-dimethyl-2(3*H*)-imidazolethione]antimony(III)

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In the structure of $AsCl_3dmit$[2a] (dmit = 1,3-dimethyl-2-(3*H*)-imidazolethione) and the structure of $AsCl_3NMe_3$,[2b] notable structural differences were observed. Both complexes

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