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Synthesis and Crystal Structure of a Salt Containing the Tritelluride(2–) Anion[1]

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The deep red compound [(4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane)potassium] tritelluride(2–)-ethylenediamine, $(C_{18}H_{36}N_2O_6K^+)_2Te_3^{2-}\cdot en$, has been prepared by the reaction of a solution of K_2Te and the ligand (2,2,2-crypt) in ethylenediamine with an excess of elemental tellurium. The compound crystallizes in the trigonal space group $P3_2$ (C_3^3, No. 145) with lattice constants $a = 12.229$ (1) and $c = 31.242$ (4) Å and three molecules per unit cell. Three-dimensional x-ray data were collected on an automated diffractometer using monochromated Mo Kα radiation. The structure was deduced by conventional heavy-atom techniques, and the positional and thermal parameters of the 61 independent nonhydrogen atoms were refined by full-matrix least squares using 2033 unique observed ($I > 3\sigma_I$) reflections to $R = 0.094$, $R_w = 0.103$. The Te_3^{2-} ion exhibits bond lengths of 2.692 (5) and 2.720 (4) Å and an angle of 113.1 (2)°. The slight deviation of Te_3^{2-} from C_{2v} symmetry together with different thermal parameters for its terminal atoms evidently arise from hydrogen bonding to the ethylenediamine molecule, $d_{Te-N} = 3.46$ (6) Å. The anion parameters are compared with those of related ions and the element.

Introduction

Although ditellurides are known in phases such as $MgTe_2$,[2] no solid containing the tritelluride group has been reported, in contrast to the existence of both trisulfides[3] and triselenides[4] in the solid state. There are several reports in the early literature of the formation of uncharacterized purple or red polytelluride species by oxidation of the telluride(2–) ion in aqueous base or by solution of the element in hydrogen telluride.[5] The stoichiometry of the ions Te_3^{2-} and Te_4^{2-} was first deduced by Kraus and Chiu[6] from an investigation of the solubility of tellurium in liquid ammonia solutions of metallic sodium. These two ions were later confirmed through potentiometric titrations by Zintl, Goubeau, and Dullenkopf[7] as part of an extensive investigation of the electrochemistry of polyanions of the post transition elements in liquid ammonia. Both reports described a variety of colors for the anions: yellow for the slightly soluble Te^{2-}, purple or blue for Te_2^{2-}, and clear deep red for Te_3^{2-} and Te_4^{2-}. Neither group of investigators isolated and characterized a solid product containing these species, although Kraus reported a metallic-appearing solid remained on evaporation of the solvent. The species Te_3^{2-} and Te_4^{2-} are isoelectronic with the two cations I_3^+ and I_4^{2+} which have been deduced in solid I_3AlCl_4 by Merryman and coworkers[8] and in HSO_3F solution by Gillespie et al.,[9] respectively. It will be shown here that, as in the case of Pb_5^{2-} and Bi_5^{3+},[10] the isoelectronic species Te_3^{2-} and I_3^+ are also isostructural.

Recently the first isolation of several other "Zintl ions" in the solid state has been reported.[10-14] In this as in most of these other studies the key to the isolation of a stable and tractable solid product has been the use of 2,2,2-crypt[15,16] to complex the alkali metal cation and thereby prevent the formation of otherwise more stable intermetallic phases, K_2Te_3 in the present system.

Experimental Section

Synthesis. The 2,2,2-crypt (Merck) was used as received from E. M. Laboratories and was handled only in the drybox. K_2Te was synthesized from potassium (J. T. Baker, "purified") and tellurium (United Mineral and Chemical, 99.999%) by precipitation from liquid ammonia solution. Stoichiometric K_2Te_3, previously reported by Klemm et al.,[18] was synthesized from K_2Te and tellurium while contained in a porcelain crucible sealed within an evacuated Vycor jacket. The apparatus was heated to 500 °C for 0.5 h and then to 700 °C for an additional 0.5 h. The resulting friable, silvery gray solid showed no evidence of either unreacted tellurium or K_2Te in its powder pattern (Debye-Scherrer).

The tritelluride anion was synthesized by reaction of stoichiometric quantities of crypt and K_2Te with excess tellurium. These were placed in one arm of a two-armed apparatus and 40–50 ml of dry ethylenediamine (en, distilled from CaH_2 and stored over Molecular Sieve) was condensed onto the mixture. The immediate result was a green solution which over a period of 3 days became first blue, then purple, and finally a deep, clear red which did not change on further standing. The solution was decanted from the excess tellurium, and triangular and hexagonal crystals were grown by evaporation of the solvent. Crystals up to several millimeters on an edge could be obtained by varying the rate of solvent evaporation. A clear deep red solution was obtained within minutes of condensing sufficient en onto solid K_2Te_3 plus crypt with no hint of either other colors or undissolved solids.

The reaction vessel was opened under a nitrogen atmosphere in a specially designed drybox[19] and crystals with dimensions of about 0.2–0.3 mm were mounted and sealed in 0.3-mm i.d. Lindemann glass capillaries. These were examined by oscillation and Weissenberg techniques, and the best diffracting specimen was mounted for data collection on an automated four-circle diffractometer designed and built in the Ames Laboratory and described in detail elsewhere.[20] The crystal had the form of a triangular pyramid with truncated corners (C_{3v} symmetry) 0.2 mm in height and 0.3 mm on basal edges.

Data Collection. Trigonal symmetry with $a = 12.26$ Å and $c = 31.33$ Å was indicated by the initial orientation,[21] and integrated intensity data were collected on this basis at a temperature of ~25 °C for $2\theta \leq 50°$ using Mo Kα radiation monochromatized with pyrolytic graphite (λ 0.709 54 Å) at a takeoff angle of 4.5°. During data collection the intensities of three different standard reflections were monitored every 75 reflections to check for instrument and crystal stability. A total of 5591 reflections were examined over the HKL and $HK\bar{L}$ octants with standard reflection decay of only about 1%. Final unit cell parameters of $a = 12.229$ (1) Å and $c = 31.242$ (4) Å were obtained from the same crystal by a least-squares fit to twice the Ω values of 14 reflections each of which was tuned on both Friedel-related peaks to eliminate instrument and centering errors. These dimensions give a volume of 4046 Å^3 and a density of 1.57 g/cm^3 for $Z = 3$ and a formula weight of 1274.10. Programs utilized were as referenced before[14,19] unless otherwise noted.

The observed intensities were corrected for Lorentz and polarization effects, but no absorption correction was made as the linear absorption coefficient was calculated to be only 18.8 cm^{-1}.[22] A total of 2385 reflections were "observed" by the criterion $I > 3\sigma_I$, and 2033 unique reflections remained after averaging of equivalent reflections. The condition $l = 3n$ for observation of $00l$ reflections indicates a threefold screw axis parallel to c and requires that the compound be in one of ten space groups which make up five enantiomeric pairs: $P3_1$ (C_3^2, No. 144) and $P3_2$ (C_3^3, No. 145), $P3_112$ (D_3^3, No. 151) and $P3_212$ (D_3^5, No. 153), $P3_121$ (D_3^4, No. 152) and $P3_221$ (D_3^6, No. 154), $P6_2$ (C_6^4, No. 171) and $P6_4$ (C_6^5, No. 172), and $P6_222$ (D_6^4, No. 180) and $P6_422$ (D_6^2, No. 181). These choices were reduced to one pair, $P3_1$ and $P3_2$, by the lack of any symmetry higher than $\bar{3}$ in the diffraction data; that is, averaging the data in the higher Laue classes $\bar{3}2/m$ and $6/m$ gave poor agreement between supposedly equivalent reflections, while in $\bar{3}$ the equivalent pairs matched quite well.

Structure Determination and Refinement. The trial structure was obtained by conventional heavy-atom techniques, the shape of the anion being readily apparent from the Patterson map. Full-matrix least-squares refinement of the tellurium and potassium atom positions

Table I. Final Positional and Thermal Parameters for $(\text{crypt-K}^+)_2\text{Te}_3^{2-}$

	Fractional coordinates			Atomic temperature factors					
Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Te(1)	0.1671 (3)	0.1585 (3)	0.0	23.2 (5)	22.2 (5)	1.56 (3)	14.6 (4)	0.9 (1)	0.6 (1)
Te(2)	0.0232 (3)	0.2221 (4)	0.0499 (1)	23.2 (5)	30.0 (6)	1.59 (4)	20.4 (5)	−0.3 (1)	−0.1 (1)
Te(3)	0.0622 (2)	0.2017 (2)	0.1349 (1)	10.9 (3)	11.6 (3)	1.75 (4)	5.3 (2)	0.45 (9)	0.20 (9)
K(1)	0.7250 (7)	0.5365 (7)	0.1244 (2)	10.6 (9)	11.5 (9)	1.22 (9)	5.5 (8)	0.2 (2)	0.2 (2)
K(2)	0.3974 (7)	0.8688 (7)	0.1646 (3)	10.2 (9)	9.8 (9)	1.6 (1)	5.6 (8)	−0.2 (2)	−0.4 (2)

	Fractional coordinates			Atomic temp factors (B), Å^2		Fractional coordinates			Atomic temp factors (B), Å^2
Atom	x	y	z		Atom	x	y	z	
N(101)[b]	0.723 (3)	0.520 (3)	0.028 (1)	6.3 (7)	C(203)	0.210 (5)	0.651 (5)	0.080 (1)	9 (1)
C(102)	0.848 (4)	0.609 (4)	0.012 (1)	7 (1)	O(204)	0.226 (2)	0.646 (2)	0.1227 (9)	6.7 (6)
C(103)	0.900 (4)	0.733 (4)	0.030 (1)	7 (1)	C(205)	0.108 (4)	0.567 (4)	0.144 (1)	7 (1)
O(104)	0.935 (2)	0.731 (2)	0.0779 (8)	6.0 (5)	C(206)	0.143 (4)	0.549 (4)	0.190 (1)	7 (1)
C(105)	0.976 (4)	0.853 (4)	0.097 (1)	7 (1)	O(207)	0.192 (2)	0.670 (2)	0.2119 (7)	5.9 (5)
C(106)	0.017 (3)	0.846 (3)	0.142 (1)	6.2 (9)	C(208)	0.228 (4)	0.655 (4)	0.255 (1)	6.7 (9)
O(107)	0.896 (2)	0.759 (2)	0.1642 (7)	5.7 (5)	C(209)	0.265 (5)	0.788 (5)	0.277 (1)	9 (1)
C(108)	0.931 (4)	0.772 (4)	0.209 (1)	6 (1)	N(210)	0.398 (3)	0.877 (3)	0.261 (1)	8.0 (9)
C(109)	0.787 (3)	0.691 (3)	0.232 (1)	6.2 (9)	C(211)	0.439 (4)	0.008 (5)	0.275 (1)	8 (1)
N(110)	0.727 (2)	0.558 (2)	0.218 (1)	5.5 (6)	C(212)	0.373 (6)	0.070 (6)	0.252 (2)	11 (1)
C(111)	0.592 (4)	0.482 (4)	0.236 (1)	7 (1)	O(213)	0.396 (2)	0.074 (2)	0.2068 (9)	6.8 (6)
C(112)	0.518 (4)	0.528 (4)	0.211 (1)	6.5 (9)	C(214)	0.332 (3)	0.126 (3)	0.185 (1)	6.1 (9)
O(113)	0.509 (2)	0.491 (2)	0.1684 (7)	5.4 (5)	C(215)	0.367 (4)	0.143 (4)	0.143 (1)	7 (1)
C(114)	0.415 (3)	0.511 (3)	0.145 (1)	5.6 (8)	O(216)	0.343 (2)	0.035 (2)	0.1208 (8)	6.5 (6)
C(115)	0.406 (3)	0.468 (3)	0.102 (1)	4.9 (7)	C(117)	0.361 (5)	0.045 (5)	0.074 (1)	9 (1)
O(116)	0.517 (2)	0.531 (2)	0.0781 (8)	5.8 (5)	C(218)	0.326 (5)	0.919 (5)	0.054 (1)	8 (1)
C(117)	0.511 (5)	0.491 (4)	0.035 (1)	8 (1)	C(219)	0.521 (5)	0.927 (4)	0.055 (1)	9 (1)
C(118)	0.631 (3)	0.553 (3)	0.010 (1)	5.6 (8)	C(220)	0.610 (4)	0.893 (4)	0.075 (1)	7 (1)
C(119)	0.682 (4)	0.389 (4)	0.018 (1)	8 (1)	O(221)	0.614 (2)	0.911 (2)	0.1205 (8)	5.9 (5)
C(120)	0.745 (4)	0.328 (5)	0.041 (1)	8 (1)	C(222)	0.701 (3)	0.888 (3)	0.140 (1)	4.9 (7)
O(121)	0.712 (2)	0.318 (2)	0.0864 (8)	5.9 (5)	C(223)	0.718 (2)	0.942 (3)	0.187 (1)	6.1 (9)
C(122)	0.783 (3)	0.268 (3)	0.111 (1)	5.3 (8)	O(224)	0.605 (2)	0.872 (2)	0.2107 (7)	5.4 (5)
C(123)	0.741 (3)	0.252 (3)	0.154 (1)	5.2 (8)	C(225)	0.615 (4)	0.903 (4)	0.256 (1)	8 (1)
O(124)	0.773 (2)	0.375 (2)	0.1734 (8)	6.2 (6)	C(226)	0.497 (4)	0.839 (4)	0.276 (1)	6 (1)
C(125)	0.758 (4)	0.362 (4)	0.219 (1)	8 (1)	N(1)(en)	0.008 (5)	0.226 (5)	0.242 (1)	11 (1)
C(126)	0.803 (4)	0.497 (4)	0.237 (1)	7 (1)	C(2)(en)	0.99 (1)	0.15 (1)	0.263 (5)	22 (5)
N(201)	0.400 (3)	0.863 (3)	0.071 (1)	7.4 (8)	C(3)(en)	0.16 (1)	0.27 (1)	0.264 (5)	25 (5)
C(202)	0.336 (4)	0.733 (4)	0.057 (1)	7 (1)	N(4)(en)	0.174 (4)	0.218 (4)	0.301 (1)	9 (1)

[a] $\beta_{ij} \times 10^3$. [b] The first digit keys the crypt molecule; the others give the atom number as in ref 14.

with isotropic thermal parameters resulted in an unweighted factor $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.22. Location of the 52 independent nonhydrogen atoms of the two crypt molecules by Fourier synthesis and refinement of their positions and isotropic temperature factors resulted in $R = 0.13$.

Examination of an electron difference map at this point revealed the presence of four peaks near the tritelluride ion arranged roughly in the manner expected for the nonhydrogen atoms of an ethylenediamine molecule. On introducing these and conversion of the tellurium and potassium atoms to anisotropic temperature factors [of the form $\exp(-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}))$] refinement of all 269 independent parameters gave $R = 0.095$ and $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ of 0.123, where w was set equal to σ_F^{-2}. Because of a strong systematic dependence of $||F_o| - |F_c||$ on $(\sin\theta)/\lambda$ and F_o the data were reweighted in 20 groups to minimize these dependences, giving final values $R = 0.094$ and $R_w = 0.103$. The largest shift in any variable during the last cycle of refinement was 0.12σ in en atoms, 0.05σ in crypt atoms, and 0.03σ in heavy atoms. A difference Fourier map indicated residuals only $<\pm 0.5$ e/Å^3 except near the tellurium atoms where they ranged to ± 0.75 e/Å^3. The 80 unlocated hydrogen atoms in this compound account for 12.5% of the total electron density and furnish a plausible explanation for R being above 0.09.

The correct resolution between the enantiometric space groups $P3_1$ and $P3_2$ was accomplished by refinement of all final parameters to convergence in both of the possible space groups, relying on the anomalous dispersion of tellurium and potassium[22] to indicate the correct choice. The result was a slight (0.0009) but consistent difference in R_w in favor of $P3_2$.

Results and Discussion

The final positional and thermal parameters are listed in Table I. Bond lengths, angles, and significant nonbonded distances for the Te_3^{2-} anion, together with bond lengths and angles for the hydrogen-bonded ethylenediamine molecule and oxygen, nitrogen, and potassium atoms of the cryptated cations, appear in Table II, with the remaining distances and angles appearing in the supplementary material. The observed and calculated structure factors are also given in the supplementary material.

The [110] view of the contents of one unit cell is shown in Figure 1. The most interesting feature of this compound is the hitherto unknown tritelluride ion, illustrated in Figure 2 in two views. The deviation of the ion from C_{2v} symmetry by 0.028 Å (4σ) is probably significant and contrasts with the rigorous C_{2v} symmetry required by crystal symmetry for the cogeneric S_3^{2-} and Se_3^{2-} anions.[2,3] This difference in bond lengths is probably the result of hydrogen bonding between Te(3) and N(1) of the ethylenediamine molecule which is 3.46 (6) Å away. Hamilton and Ibers[24] suggested that evidence of a hydrogen bond in a crystalline salt is the observation of a distance between two nonhydrogen atoms, one of which is capable of donating electrons (tellurium in this case) and one of which is electronegative and bonded to hydrogen, which is less than the sum of the van der Waals radii. This sum is 3.70 Å according to Pauling,[25] or 0.24 Å greater than the observed distance. Because this is a rather large reduction from the expected distance and because the 2.20-Å value for the tellurium(2−) radii may be inappropriately large for present purposes,[26] another estimate of the radii by Bondi[27] was also used. These values (2.06 and 1.55 Å) still sum to a distance 0.15 Å greater than that measured, giving definite evidence of a hydrogen bond. Such a basicity for Te_3^{2-} was unexpected,

Table II. Distances and Angles

Atom 1	Atom 2	Dist, Å	Dist averaged for thermal motion, Å	Atom 1	Atom 2	Dist, Å
Te(1)	Te(2)	2.692 (5)	2.782 (5)	K(2)	N(201)	2.91 (4)
Te(2)	Te(3)	2.720 (4)	2.790 (4)	K(2)	O(104)	2.79 (3)
Te(3)	N(1)(en)	3.46 (6)		K(2)	O(107)	2.88 (3)
Te(1)	Te(3)	4.516 (4)		K(2)	N(110)	3.02 (4)
Te(3)	Te(1)′	7.456 (5)		K(2)	O(113)	2.85 (3)
K(1)	N(101)	2.99 (4)		K(2)	O(116)	2.80 (3)
K(1)	O(104)	2.88 (3)		K(2)	O(121)	2.80 (3)
K(1)	O(107)	2.76 (3)		K(2)	O(124)	2.91 (3)
K(1)	N(110)	2.95 (3)		N(1)(en)	C(2)(en)	1.04 (16)
K(1)	O(113)	2.77 (3)		C(2)(en)	C(3)(en)	1.85 (20)
K(1)	O(116)	2.89 (3)		C(3)(en)	N(4)(en)	1.40 (17)
K(1)	O(121)	2.85 (3)				
K(1)	O(124)	2.78 (3)				

Atom 1	Vertex atom 2	atom 3	Angle, deg	Atom 1	Vertex atom 2	Atom 3	Angle, deg
Te(1)	Te(2)	Te(3)	113.1 (2)	N(201)	K(2)	N(210)	179.1 (10)
Te(3)	N(1)(en)	C(2)(en)	121 (5)	N(201)	K(2)	O(204)	61.4 (9)
N(101)	K(1)	N(110)	178.5 (12)	N(201)	K(2)	O(216)	62.5 (8)
N(101)	K(1)	O(104)	61.7 (8)	N(201)	K(2)	O(221)	59.4 (11)
N(101)	K(1)	O(116)	61.5 (10)	N(210)	K(2)	O(207)	60.1 (8)
N(101)	K(1)	O(121)	61.7 (10)	N(210)	K(2)	O(213)	59.2 (9)
N(110)	K(1)	O(107)	59.5 (7)	N(210)	K(2)	O(224)	61.0 (11)
N(110)	K(1)	O(113)	59.2 (9)	O(204)	K(2)	O(216)	98.5 (9)
N(110)	K(1)	O(124)	61.5 (10)	O(216)	K(2)	O(221)	100.0 (8)
O(104)	K(1)	O(116)	100.1 (8)	O(221)	K(2)	O(204)	91.3 (9)
O(116)	K(1)	O(121)	97.7 (9)	O(207)	K(2)	O(213)	97.0 (9)
O(121)	K(1)	O(104)	100.0 (9)	O(213)	K(2)	O(224)	98.6 (9)
O(107)	K(1)	O(113)	98.5 (8)	O(224)	K(2)	O(207)	98.3 (8)
O(113)	K(1)	O(124)	96.1 (9)				
O(124)	K(1)	O(107)	97.3 (9)				

Table III. Bond Lengths and Bond Angles in Some Catenated Compounds of Group 6 Elements

	Te_3^{2-}	Se_3^{2-}	S_3^{2-}	I_3^+	Te	Se	S	Te_2^{2-}	Te_4^{2+}	Se_4^{2+}
Bond lengths, Å	2.692 (5) 2.720 (4)	2.40 (5)	2.076 (5)	*a*	2.835 (2)	2.373 (5)	2.047 (3)[c]	2.70 (1)	2.674 (2) 2.663 (2)	2.286 (4) 2.280 (4)
Bond angle, deg	113.1 (2)	110 (3)	114.9 (4)	97[b]	103.2 (1)	103.1 (2)	108.1 (1)[c]		*d*	*d*
Compd	$(crypt\text{-}K)_2\text{-}Te_3\cdot en$	$BaSe_3$	BaS_3	I_3AlCl_4	Te	Trigonal Se	S_8	$MgTe_2$	$Te_4(AlCl_4)_2$	$Se_4(HS_2O_7)_2$
Ref	This work	4	3	8	28	29	30	31	26	32

[a] Not known. [b] Based on NQR spectrum analysis. [c] Average of four values. [d] Not comparable as ion is square planar.

however. The substantial differences in thermal parameters of the two end tellurium atoms also indicate the presence of the hydrogen bond. Those for Te(3) which participates in this bond are only about half the size found for the other two atoms and more nearly approximate a sphere, as seen in Figure 2(b). Thus the motion of Te(3) does appear more restricted, as would be expected with the additional bonding. The presence of only this hydrogen bond from the en molecule is in turn presumably responsible for the relatively large positional uncertainties and thermal parameters found, especially for the carbon atoms. There is no evidence for more than one conformation in the crystal, but random disorder and true thermal motion may both contribute.

Table III lists bond lengths and angles for a number of species which may be compared with the tritelluride ion. The isoelectronic I_3^+ ion has not been structurally well characterized but the 97° bond angle estimated on the basis of its ^{127}I NQR spectrum[8] is distinctly smaller. Although some doubts could be raised regarding the simple bonding model used in analysis of the latter, the trend may be real as ICl_2^+ shows a comparable angle. Some opening of the angle would be expected for the higher charged Te_3^{2-}.

Both angles and distances in Te_3^{2-}, Se_3^{2-}, and S_3^{2-} are reasonable when account is taken of the lower precision of the Se_3^{2-} (powder) data. In the stable elemental forms selenium and tellurium are isostructural, consisting of infinite helices of atoms parallel to the trigonal *c* axis. The M_3^{2-} ions may be considered as three-atom pieces of that chain, with the bonds at both ends reduced to complete the lone pair and furnish the charge. In the same way, S_3^{2-} could be formed from part of a S_8 ring. A comparison of bond angles between the ions and the elements indicates considerable consistency: S_3^{2-} has an angle 7° greater than S_8, Se_3^{2-}, about 7 ± 3° greater than in elemental selenium, and Te_3^{2-}, 10° greater than in the element. The bond lengths present a different story however; the bond length in S_3^{2-} is only 0.03 Å greater than S_8; for selenium, the difference is less than the standard deviation of 0.05 Å in the bond length in Se_3^{2-}, but with tellurium the average of the bond lengths in Te_3^{2-} is 0.129 (5) Å *less* than in the element. This contraction is not really surprising when the structure of elemental tellurium is considered in more detail. Each atom therein has, in addition to its two nearest "bonded" neighbors at 2.835 (2) Å, four other atoms 3.495 (3) Å away in other chains, close enough to suggest some form of bonding interaction which completes a distorted octahedron around each atom.[33] This secondary bonding, present in tellurium but virtually absent in the isostructural selenium, is not surprising considering the more

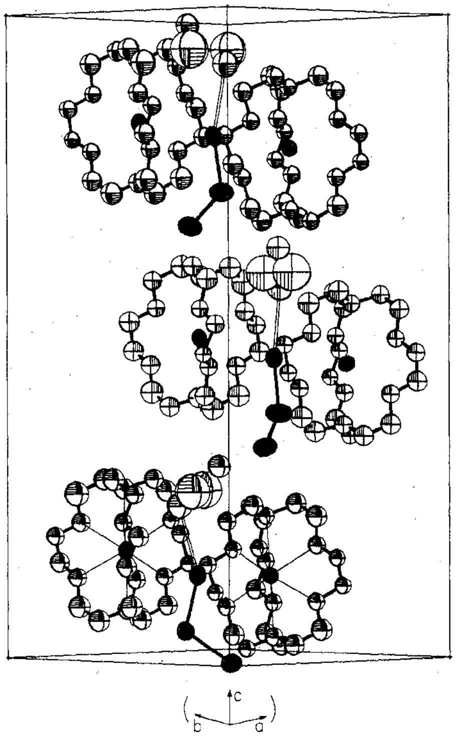

Figure 1. The [110] view of the unit cell of (crypt-K$^+$)$_2$Te$_3^{2-}$. Tellurium and potassium atoms are darkened.

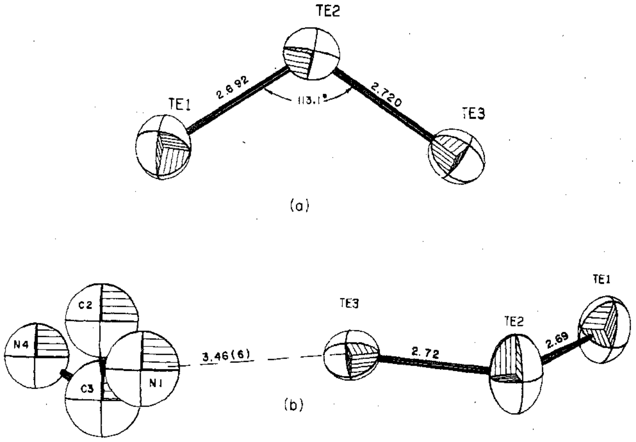

Figure 2. Details of the Te$_3^{2-}$ ion in (crypt-K$^+$)$_2$Te$_3^{2-}$: (a) normal view; (b) approximately coplanar view showing the hydrogen-bonded ethylenediamine molecule.

metallic character of tellurium and appears to lower the bond order within the helical chain with a resulting increase in bond length.

Two other bonds to which Te$_3^{2-}$ can be compared are those in Te$_2^{2-}$ and Te$_4^{2+}$. The former (isoelectronic with I$_2$) is quite comparable in distance in MgTe$_2$ (2.70 (1) Å) and not greatly different in MnTe$_2$ at 2.74 (3) Å.[34] The tetratellurium(2+) cation has a bond order of 1.25 and appropriately contains bonds 0.038 Å shorter than the presumed single bonds in Te$_3^{2-}$. For selenium, Se$_3^{2-}$ has bonds 0.12 Å longer than those of Se$_4^{2+}$, but the large standard deviation for the anion makes it impossible to tell if the magnitude of this difference is significant.

The two cryptated potassium cations found are essentially the same as dealt with in some detail elsewhere[35] and will not be discussed at length here. There are two variations from that work however: first, a slight, but definite trend to generally longer bonds and, second, a slight (0.04 Å, 1σ) shift of the potassium atom toward one end of the ligand in the present symmetry-unconstrained crypt cations relative to those reported earlier with a twofold symmetry axis normal to the N-K-N axis.

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Registry No. (crypt-K$^+$)$_2$Te$_3^{2-}$·en, 61520-77-2.

Supplementary Material Available: Listings of structure factor amplitudes and additional bond distances and angles (10 pages). Ordering information is given on any current masthead page.

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