Figure 2. The $(\mu\text{-H})_2Os_3(CO)_{10}$ molecule projected onto its Os$_3$ plane (ORTEP-II diagram; 50% probability ellipsoids).

(7)° while the adjacent angles, Os(2)–Os(1)–C(12) and Os(3)–Os(1)–C(11), have values of 106.6 (5) and 98.4 (5)°, respectively. This result is not too surprising since the μ-bridging hydride ligands are, of course, each appreciably displaced from the equatorial plane (cf. Figure 1) and will be involved in little repulsive interaction with the adjacent equatorial carbonyl ligands.

The molecule has approximate C_{2v} symmetry and there are, therefore, four chemically distinct locations for the carbonyl ligands. The mutually trans axial carbonyl ligands on Os(1) have the longest osmium–carbon distances [Os(1)–C(13) = 1.950 (14) Å and Os(1)–C(14) = 1.957 (14) Å], while the mutually cis equatorial ligands are associated with shorter osmium–carbon bond lengths [Os(1)–C(11) = 1.913 (16) Å and Os(1)–C(12) = 1.898 (16) Å]. This pattern is expected, since competition for back-donated π-electron density is severe for mutually trans π-acceptor ligands and minimal for carbonyl ligands trans to single metal–metal bonds. Similar patterns have been determined for Os$_3$(CO)$_{12}$ [Os–CO(axial) = 1.946 (6) Å and Os–CO(equatorial) = 1.912 (7) Å][1] and for Ru$_3$(CO)$_{12}$ [Ru–CO(axial) = 1.942 (4) Å and Ru–CO(equatorial) = 1.921 (5) Å].[16]

The remaining group-theoretically distinct sets of carbonyl groups consist of (1) the equatorial ligands adjacent to the

Os$(\mu\text{-H})_2$Os system, which are characterized by the bond lengths Os(2)–C(21) = 1.914 (18) Å and Os(3)–C(31) = 1.934 (18) Å, and (2) the set of four semiaxial ligands which are trans to the bridging hydride ligands, in which Os(2)–C(22) = 1.917 (14) Å, Os(2)–C(23) = 1.900 (15) Å, Os(3)–C(32) = 1.887 (15) Å, and Os(3)–C(33) = 1.922 (15) Å.

The Os–C–O systems are all, as expected, close to linear, with individual values ranging from Os(2)–C(23)–O(23) = 174.2 (15)° to Os(1)–C(11)–O(11) = 179.8 (14)°. The carbon–oxygen distances range from 1.113 (19) to 1.151 (23) Å.

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Registry No. $(\mu\text{-H})_2Os_3(CO)_{10}$, 41766-80-7.

Supplementary Material Available: Listing of structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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The Crystal Structure of Tetrakis(ethylenethiourea)tellurium(II) Chloride Dihydrate: A Novel (+–+–) Square-Planar Conformer

R. C. ELDER,* T. MARCUSO, and P. BOOLCHAND

The structure of [Te(ethylenethiourea)$_4$]Cl$_2$·2H$_2$O has been determined using single-crystal x-ray diffraction. The crystal is of the monoclinic class, a = 18.70 (3), b = 7.82 (1), c = 18.34 (3) Å, β = 109.3 (1)°. The space group has been reassigned as $P2/n$. The 2654 reflections were used to refine the structure by least squares to R_1 = 0.039 and R_2 = 0.058. The structure contains two independent [Te(etu)$_4$]$^{2+}$ cations with nearly square-planar coordination of tellurium by sulfur. A new type of conformational isomer has been observed in which adjacent etu ligands are alternately oriented up and down with respect to the TeS$_4$ plane. The notation (+–+–) is proposed to designate such an isomer. Comparisons are made to 15 previously determined TeS$_4$, TeS$_2$Se$_2$, and TeSe$_4$ complexes all of which have the ++–– conformation.

Introduction

Cheyne and Jones[1-3] have recently published a series of papers on the Mössbauer spectra of complexes of tellurium with thiourea (tu) and related derivatives. From single-crystal

spectra they were able to assign a negative nuclear quadrupole moment to the $^3/_2$ excited state in ^{125}Te. From the work of Foss[4] and his school, Te(II)S$_4$ systems are known to form quite regular square-planar complexes and both the structural and Mössbauer results may be interpreted in terms of a stereochemically inert 5s^2 electron pair and pure 5p bonding. Due to the early date at which many of the structural analyses were

* To whom correspondence should be addressed at the Department of Chemistry.
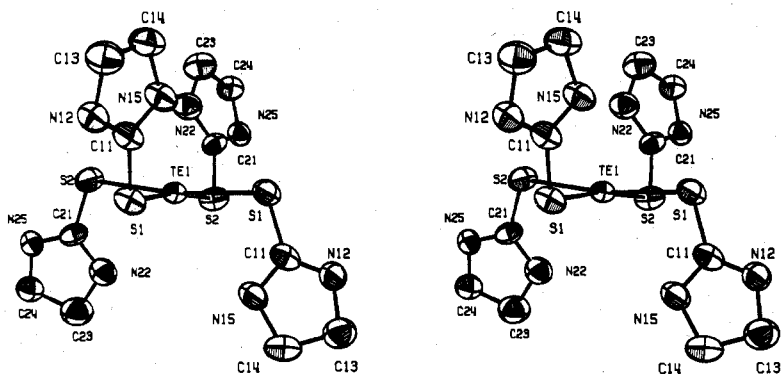
Figure 1. A stereoscopic view of one of the two independent [Te(etu)₄]²⁺ cations. The twofold axis passes through the tellurium atom approximately normal to the plane of the drawing.

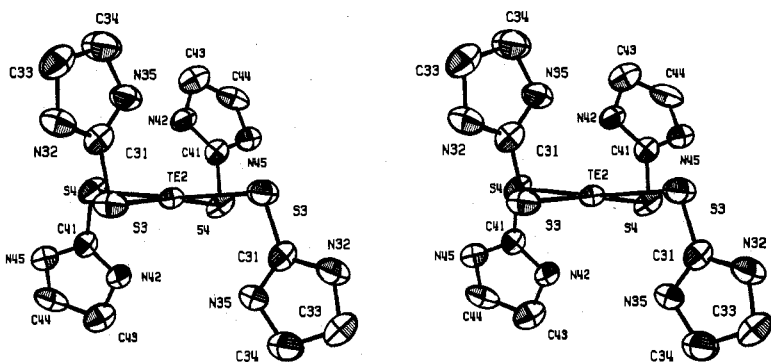**Figure 2.** A stereoscopic view of the second independent [Te(etu)₄]²⁺ cation.

performed, the results are not extremely precise. Since we are examining the Mössbauer spectra of a series of related compounds, we have determined the structure of [Te-(etu)₄]Cl₂·2H₂O (etu = ethylenethiourea, C₃H₆N₂S). This structure, which we report here, exhibits an entirely different conformation of the sulfur ligands about tellurium from that observed previously.

Experimental Section

Yellow needles of the title compound were prepared in a manner similar to that of Foss and Fossen.[5] Some difficulty with precipitation of metallic tellurium occurred if the solutions were held above 60 °C for more than a few hours. The crystals used in the x-ray study were recrystallized from 4 N hydrochloric acid (40 °C) by slow cooling to room temperature. The crystals were washed with 2 N hydrochloric acid, ethanol, and ether and air dried. A crystal 0.18 × 0.23 × 0.34 mm was mounted parallel to the long dimension on Syntex P1̄ diffractometer, equipped with a graphite crystal monochromator. Unit cell constants and intensity data were obtained in the usual manner.[6] A preliminary survey of the intensity data indicated that it could be indexed in accord with the published unit cell constants and space group assignment (a = 18.22 (9), b = 7.84 (4), c = 21.30 (11) Å, β = 124.0 (6)°, space group P2₁/c).[5] Our measurements for the equivalent cell gave a = 18.34 (3), b = 7.82 (1), c = 21.43 (4) Å, β = 124.6 (1)° with systematic absences h0l, l = 2n + 1, and 0k0, k = 2n + 1. In order to obtain a β angle closer to 90.0°, we chose the alternate cell, with a = 18.70 (3), b = 7.82 (1), c = 18.34 (3) Å, β = 109.3 (1)°. In this cell the systematic absences became h0l, h + l = 2n + 1, and 0k0, k = 2n + 1, and thus the space group was assigned as P2₁/n.

Intensity measurements were made for 3115 unique reflections within the sphere 2θ < 44°. Of these, 2654 had I > 2σ(I), where 0.04 was used for p in the previously defined[6] weighting scheme. The θ/2θ scan was from 0.9° below to 1.1° above the reflection in 2θ. Scan rates were varied from 2.0 to 8.0°/min depending on the intensity of the reflection. Crystal quality was checked (partial rotation photographs about each of the three axes, mosaic scans) and standards were measured to check stability. Absorption corrections[7] were applied since μ = 17.33 cm⁻¹. The calculated transmission coefficients ranged from 0.65 to 0.79. For this crystal there are four molecules in the

unit cell (d_calcd = 1.69, d_meas = 1.66 (3) g cm⁻³, neutral buoyancy CHCl₃/CH₂Br₂).

Solution and Refinement of the Structure. A Patterson synthesis[8] yielded Te–Te and Te–S vectors from which tellurium and sulfur atom positions were deduced. Subsequent electron density syntheses allowed the location of all other non-hydrogen atoms. However, this model was plagued by chemically unreasonable bond distances and, with isotropic thermal parameters for all non-hydrogen atoms, would not refine below R₁ ≃ 0.25.[9] A careful re-examination of the intensity data indicated that the 0k0, k = 2n + 1, reflections were weak but not absent. A solution utilizing Te–Te, Te–S, and S–S vectors was found from the Patterson synthesis for the space group P2/n with two tellurium atoms each on a twofold axis. The subsequent electron density map indicated positions for all non-hydrogen atoms except two carbon atoms which appeared on the next map. The structure quickly refined using isotropic thermal parameters to R₁ = 0.077. C–H distances were fixed at 0.97 Å, N–H distances at 0.87 Å, H–C–H angles at 109.5°, and isotropic[10] H-atom temperature parameters at U = 0.05 Å². Refinement of non-hydrogen atom positional and anisotropic temperature parameters converged[11] with R₁ = 0.039 and R₂ = 0.058. In the last cycle of refinement the maximum shift/error was 0.2 and the average shift/error was 0.03. The neutral atom scattering curves of Cromer[12] were used for Te, S, Cl, O, N, and C. Those of Stewart[13] were used for hydrogen. Corrections for anomalous dispersion[14] were made as follows: Te, Δf′ = 0.772, Δf″ = 1.675; S, Δf′ = 0.110, Δf″ = 0.124; and Cl, Δf′ = 0.132, Δf″ = 0.159. Hydrogen atoms were not found for the water molecules.

Due to the large variation in the Te–S bond lengths (vide infra), calculations were attempted in space group Pn for each possible enantiomer. These calculations did not significantly improve R₁, nor did they lead to more similar values for the Te–S bond lengths. Therefore we report the results of refining 263 parameters with 2654 reflections in space group P2/n. The values of |F_o| and F_c are available as Table A.[15]

Results and Discussion

The fractional atomic positional parameters and the anisotropic thermal parameters for the non-hydrogen atoms are presented in Table I. Those calculated for hydrogen atom positions are in Table B.[15] The structures of the two independent cations are illustrated in Figures 1 and 2. Bond

Table I. Fractional Atom Coordinates[a] ($\times 10^4$) and Anisotropic Thermal Parameters[b] ($A^2 \times 10^3$)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Te(1)	2500[c]	5455 (1)	2500	30 (1)	31 (1)	32 (1)	0[d]	9 (1)	0
Te(2)	2500	0380 (1)	7500	31 (1)	35 (1)	30 (1)	0	7 (1)	0
S(1)	2177 (1)	7895 (2)	3387 (1)	50 (1)	45 (1)	39 (1)	12 (1)	7 (1)	−8 (1)
S(2)	3013 (1)	3105 (2)	1753 (1)	39 (1)	48 (1)	58 (1)	5 (1)	17 (1)	−15 (1)
S(3)	1721 (1)	2788 (2)	8021 (1)	57 (1)	54 (1)	38 (1)	16 (1)	10 (1)	−8 (1)
S(4)	1644 (1)	−1972 (2)	7794 (1)	33 (1)	51 (1)	57 (1)	−4 (1)	7 (1)	19 (1)
Cl(1)	0025 (1)	5942 (2)	8743 (1)	56 (1)	68 (1)	55 (1)	0 (1)	31 (1)	−4 (1)
Cl(2)	1145 (1)	1359 (3)	4902 (1)	53 (1)	89 (2)	63 (1)	−9 (1)	34 (1)	−5 (1)
N(12)	0858 (3)	9486 (6)	3196 (3)	50 (4)	48 (4)	41 (3)	14 (3)	22 (3)	−3 (3)
N(15)	0968 (3)	8643 (8)	2120 (3)	55 (4)	59 (4)	37 (4)	11 (3)	9 (3)	−8 (3)
N(22)	1533 (3)	2297 (7)	1010 (3)	55 (4)	60 (4)	51 (4)	−4 (3)	22 (3)	−21 (3)
N(25)	2321 (2)	1441 (7)	0436 (3)	45 (4)	46 (4)	36 (3)	2 (3)	25 (3)	−8 (3)
N(32)	0397 (4)	4263 (7)	7269 (3)	67 (5)	52 (4)	36 (4)	6 (3)	20 (3)	−8 (3)
N(35)	0906 (3)	3138 (8)	6489 (3)	53 (4)	85 (5)	32 (3)	22 (3)	19 (3)	−6 (3)
N(42)	2910 (3)	−3007 (8)	8953 (3)	36 (4)	80 (5)	43 (3)	−6 (3)	14 (3)	19 (3)
N(45)	1850 (3)	−3505 (7)	9124 (3)	45 (3)	47 (4)	45 (3)	6 (3)	15 (3)	2 (3)
O(1)	0657 (3)	−1360 (7)	5910 (3)	60 (3)	98 (4)	74 (4)	17 (3)	23 (3)	24 (3)
O(2)	0863 (3)	6805 (6)	0598 (3)	78 (4)	64 (4)	67 (4)	−17 (3)	14 (3)	−6 (3)
C(11)	1296 (4)	8724 (8)	2884 (3)	50 (4)	29 (4)	38 (4)	−8 (4)	6 (4)	−1 (3)
C(13)	0179 (4)	10251 (8)	2635 (4)	55 (5)	56 (5)	62 (5)	16 (4)	19 (4)	−4 (4)
C(14)	0203 (4)	9403 (9)	1898 (4)	46 (5)	59 (6)	59 (5)	2 (4)	−3 (4)	20 (4)
C(21)	2260 (3)	2256 (8)	1034 (4)	32 (4)	32 (4)	55 (4)	4 (3)	19 (3)	15 (3)
C(23)	1046 (4)	1562 (10)	0283 (5)	56 (5)	76 (6)	72 (5)	−15 (5)	18 (4)	20 (5)
C(24)	1599 (4)	0730 (9)	−0051 (4)	48 (5)	56 (5)	51 (4)	−5 (4)	19 (4)	−5 (4)
C(31)	0985 (4)	3397 (8)	7222 (4)	40 (4)	29 (4)	55 (5)	3 (3)	22 (4)	−4 (3)
C(33)	−0135 (4)	4731 (9)	6511 (4)	41 (5)	63 (5)	75 (6)	17 (4)	18 (4)	16 (4)
C(34)	0187 (5)	3773 (11)	5984 (4)	74 (6)	85 (6)	46 (4)	26 (5)	16 (4)	4 (5)
C(41)	2165 (4)	−2843 (8)	8653 (4)	40 (4)	28 (4)	46 (4)	−8 (3)	27 (4)	0 (3)
C(43)	3155 (4)	−3742 (11)	9730 (4)	57 (5)	67 (6)	70 (6)	4 (5)	13 (4)	8 (5)
C(44)	2412 (5)	−4451 (9)	9756 (4)	88 (7)	57 (5)	33 (4)	−6 (4)	18 (4)	3 (3)

[a] The estimated errors in the last digit are given in parentheses. This form is used throughout. [b] The form of the anisotropic thermal parameters is $\exp[-2\pi^2(a^{*2}U_{11}h^2 + \ldots + 2b^*c^*U_{23}kl)]$. [c] The parameters x and y are constrained for the tellurium atoms which lie on the twofold axes and thus have no associated errors. [d] Constrained to zero by symmetry.

Table II. Bond Lengths (A)

Te(1)-S(1)	2.702 (3)	Te(1)-S(2)	2.654 (3)
Te(2)-S(3)	2.737 (3)	Te(2)-S(4)	2.609 (3)
	Av Te-S 2.675 (56)		
S(1)-C(11)	1.726 (7)	S(2)-C(21)	1.712 (6)
S(3)-C(31)	1.713 (6)	S(4)-C(41)	1.696 (6)
	Av S-C 1.712 (12)		
C(11)-N(12)	1.289 (10)	C(11)-N(15)	1.333 (8)
C(21)-N(22)	1.346 (9)	C(21)-N(25)	1.305 (9)
C(31)-N(32)	1.318 (10)	C(31)-N(35)	1.317 (9)
C(41)-N(42)	1.324 (8)	C(41)-N(45)	1.303 (10)
	Av C(sp^2)-N 1.317 (18)		
N(12)-C(13)	1.472 (8)	C(14)-N(15)	1.476 (10)
N(22)-C(23)	1.461 (9)	C(24)-N(25)	1.461 (8)
C(32)-C(33)	1.463 (9)	C(34)-N(35)	1.445 (9)
N(42)-C(43)	1.462 (10)	C(44)-N(45)	1.478 (8)
	Av N-C(sp^3) 1.465 (11)		
C(13)-C(14)	1.519 (12)	C(23)-C(24)	1.511 (12)
C(33)-C(34)	1.498 (12)	C(43)-C(44)	1.512 (12)
	Av C-C 1.510 (9)		

Table III. Bond Angles (deg)

|			
S(1)-Te(1)-S(2)	172.1 (1)	S(3)-Te(2)-S(4')[a]	172.0 (1)
S(1)-Te(1)-S(1')	90.2 (1)	S(3)-Te(2)-S(4)	88.8 (1)
S(1)-Te(1)-S(2')	89.2 (1)	S(3)-Te(2)-S(3')	93.1 (1)
S(2)-Te(1)-S(2')	92.4 (1)	S(4)-Te(2)-S(4')	90.4 (1)
S(2)-Te(1)-S(1')	89.2 (1)	S(4')-Te(2)-S(3')	88.8 (1)
Te(1)-S(1)-C(11)	107.9 (2)	Te(2)-S(3)-C(31)	105.2 (3)
Te(1)-S(2)-C(21)	108.6 (3)	Te(2)-S(4)-C(41)	105.7 (3)
S(1)-C(11)-N(12)	124.7 (5)	S(3)-C(31)-N(32)	122.6 (5)
S(1)-C(11)-N(15)	124.8 (6)	S(3)-C(31)-N(35)	128.1 (6)
S(2)-C(21)-N(22)	125.6 (5)	S(4)-C(41)-N(42)	128.8 (6)
S(2)-C(21)-N(25)	123.9 (5)	S(4)-C(41)-N(45)	109.3 (5)
C(11)-N(12)-C(13)	113.9 (6)	N(12)-C(13)-C(14)	99.9 (6)
C(21)-N(22)-C(23)	109.9 (6)	N(22)-C(23)-C(24)	103.6 (6)
C(31)-N(32)-C(33)	112.7 (6)	N(32)-C(33)-C(34)	101.3 (6)
C(41)-N(42)-C(43)	113.0 (6)	N(42)-C(43)-C(44)	100.3 (6)
C(13)-C(14)-N(15)	104.0 (5)	C(14)-N(15)-C(11)	109.8 (6)
C(23)-C(24)-N(25)	102.0 (6)	C(24)-N(25)-C(21)	112.3 (6)
C(33)-C(34)-N(35)	104.2 (5)	C(34)-N(35)-C(31)	111.7 (6)
C(43)-C(44)-N(45)	102.4 (6)	C(44)-N(45)-C(41)	111.0 (6)

[a] Primed atoms are generated from unprimed by a twofold rotation operation.

lengths and bond angles are given in Tables II and III.

Conformational Isomers. For each $[Te(etu)_4]^{2+}$ cation, two of the ethylenethiourea ligands are above the TeS_4 plane and two are below, viz.,
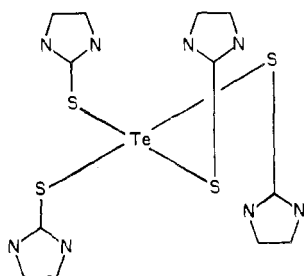
Since each of these ligands could have an up (+) or a down (−) conformation with respect to the TeS_4 plane, there are four possible isomers:
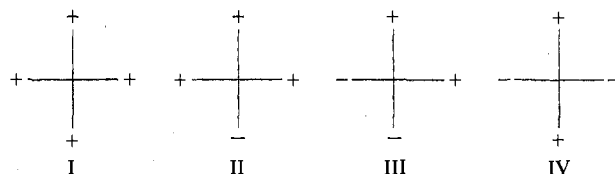
In I all four ligands are on the same side of the TeS_4 plane (++++), whereas in II one ligand is on the opposite side from the other three (+++−). In both III (++−−) and IV (+−+−),

two ligands are up and two are down; however, the steric interactions of any ligand with the ligands cis[16] to it are different in III and IV. In III each ligand has one cis neighbor on the same side and one cis neighbor on the opposite side of the TeS_4 plane, whereas in IV each ligand has both cis neighbors on the opposite side. These isomeric possibilities will occur whenever a square-planar complex has an equilibrium configuration in which the bulk of the ligand lies above or below the coordination plane.

It appears that for I and II the steric crowding will be severe and these conformations are unlikely to be observed. III and IV are less crowded than I and II and both might be expected to occur. However, based on the simplest view of internal steric interactions, IV would appear to be preferred.

Both of the independent $[Te(etu)_4]^{2+}$ cations in the title compound adopt IV. Foss and co-workers at Bergen have determined a large number of TeS_4, TeS_2Se_2, and $TeSe_4$ structures in which such conformational isomerism is possible. However, they have never commented on this possibility. These structures have included $[Te(tu)_4]Cl_2$ and $[Te(tu)_4]$-$Cl_2 \cdot H_2O$,[17] where tu = thiourea; *trans*-$[Te(tmtu)_2(tu)_2]^{2+}$ as the chloride and bromide salts,[18] where tmtu = tetramethylthiourea; *trans*-$Te(etu)_2(SCN)_2$; *trans*-$Te(etu)_2$-$(SeCN)_2$;[19] *trans*-$Te(trtu)_2(SeCN)_2$, where trtu = trimethylenethiourea; *trans*-$Te(tmtu)_2(SeCN)_2$;[20] *trans*-Te-$(tmtu)_2(S_2O_2C_6H_5)_2$;[21] two crystalline forms of *trans*-Te-$(etu)_2(S_2O_2CH_3)_2$;[22] *trans*-$Te(etu)_2(S_2O_2C_6H_5)_2$;[23] *trans*-$Te(tu)_2(S_2O_2CH_3)_2$;[24] *trans*-$Te(trtu)_2(S_2O_2C_6H_5)_2$;[25] and $[Te(su)_4]Cl_2$,[26] where su = selenourea.

Surprisingly, *in each of these 15 crystal structures the tellurium complex adopts conformation III*. Further, Foss[4] reports that seven other salts of $[Te(tu)_4]^{2+}$, six salts of $[Te(etu)_4]^{2+}$, and two salts of $[Te(trtu)_4]^{2+}$ have been examined and that for 11 of these 15 salts the tellurium atom lies on a center of symmetry which requires a ++−− conformation, III.

However, many of these assignments are based on the choice of space group $P2_1/c$. Since the difference between that choice and $P2/c$ is dependent on a class of systematic absences ($0k0$, $k = 2n + 1$) for which perhaps only eight or ten observations are available, such space group assignments should be carefully reconfirmed.

It is not clear why all of these complexes whose structures have been determined previously should adopt the ++−− conformation. For some of them, especially those of the *trans*-$Te(etu)_2(S_2O_2R)_2$ type,[22,23] internal hydrogen bonds between the two types of ligand appear to stabilize conformation III.

For others, e.g., ++−− *trans*-$[Te(tu)_2(tmtu)_2]^{2+}$,[18] no such internal hydrogen bonding occurs. The last compound appears very crowded. In fact Foss[27] has ascribed his inability to synthesize $[Te(tmtu)_4]^{2+}$ to the fact that it may be too crowded to be stable. Yet $[Te(tu)_2(tmtu)_2]^{2+}$ retains conformation III rather than the apparently less crowded IV.

It may be that +−+− $[Te(etu)_4]^{2+}$ adopts IV for an entirely different reason than internal steric crowding. Hydrogen bonding and crystal packing forces might be determinative. The recently reported[28] structure of $[Au(etu)_2]^+$ provides such a case. The complex is nearly linear (S−Au−S, 167.1°) but both etu ligands are on the same side of the gold atom, that is, the etu ligands have the same stereochemical arrangement as a pair of trans ligands in +−+− $[Te(etu)_4]^{2+}$. In the case of the gold complex the "unexpected" ligand stereochemistry is stabilized by hydrogen bonding from each of the etu ligands to the oxygen atom of a water molecule between them and centered above the gold atom. No similar arrangement exists for +−+− $[Te(etu)_4]^{2+}$. Possible hydrogen bonds are detailed in Table IV. For each of the independent cations one of the

Table IV. Possible Hydrogen Bonds (A)

Cl(1)–N(32)	3.28	Cl(2)–N(12)[e]	3.33
Cl(1)–N(45)[a]	3.28	Cl(2)–N(25)[f]	3.13
Cl(1)–O(2)[b]	3.19	Cl(2)–O(1)	3.14
Cl(1)–O(2)[c]	3.31	Cl(2)–O(1)[g]	3.20
O(1)–N(42)[d]	2.91	O(2)–N(15)	3.09

[a] Generated from the atom at x, y, z by the operation $x, 1 + y, z$. *[b]* $-x, 1-y, 1-z$. *[c]* $x, y, 1 + y$. *[d]* $1/2 - x, y, 3/2 - z$. *[e]* $x, -1 + y, z$. *[f]* $1/2 - x, y, 1/2 - z$. *[g]* $-x, -y, 1 - z$.

interior nitrogen atoms, N(15) and N(42), forms a hydrogen bond to the oxygen atom of one of the lattice water molecules. However, the other interior nitrogen atoms, N(22) and N(35), are more than 3.5 Å distant from either the oxygen atoms or the chloride anions. All four exterior nitrogen atoms appear to form weak hydrogen bonds to chloride anions.

Distortion of the TeS_4 Core. As can be seen in the figures, the arrangement of the four sulfur atoms around the tellurium atom is slightly distorted from planarity toward a tetrahedral geometry. The least-squares planes for the TeS_4 cores have been calculated and the distances of the sulfur atoms from these planes are as follows: cation Te(1), S(1) 0.182, S(1′) −0.182, S(2) 0.182, S(2′) −0.181 Å; cation Te(2), S(3) 0.179, S(3′) −0.178, S(4′) 0.192, S(4) −0.191 Å, where the primed atoms are generated from the unprimed atoms by rotation about the twofold axis passing through the tellurium atom. This slight distortion toward tetrahedral geometry, which results in trans S−Te−S angles of 172.1 (1) and 172.0 (1)°, is such that the trans etu ligands are moved away from each other.

A more significant distortion is seen in the variation of the Te−S bond lengths from 2.609 (3) to 2.737 (3) Å. Each cation has two long and two short bonds. Such a result is not particularly surprising in view of the postulated[4] bonding mechanism for these complexes which utilizes pure 5p orbitals on tellurium to form three-center, four-electron bonds to the trans sulfur atoms. The Te−S bond order is less than one and these bonds are weak and easily deformed. As one Te−S bond is elongated the trans Te−S bond is expected to shorten and the sum of the two lengths should remain relatively constant. These sums in +−+− $[Te(etu)_4]$ are 5.356 (4) and 5.346 (4) Å. For trans etu ligands in conformation III complexes, the values of these sums have ranged from 5.302 (8)[19] to 5.426 (8) Å[23] and the average for seven such sums is 5.362 (29) Å. For unsymmetrical TeS_4 systems with bidentate ligands the variation in Te−S bond lengths is much greater, e.g., Te(ethylxanthate)₂,[29] 2.49 (1), 2.48 (1), 2.90 (2), 2.86 (1) Å; Te(morpholylcarbodithioate)₂,[30] 2.498 (7), 2.530 (6), 2.856 (8), 2.834 (9) Å.

Conclusion

This structure is strikingly different from the 15 structures determined previously by Foss and co-workers. A new type of conformational isomer has been observed and there are significant distortions of a TeS_4 core with all sulfur ligands identical. However, there can be little doubt concerning the accuracy of the present results for several reasons: (a) the relatively low values of $R_1 = 0.039$ and $R_2 = 0.058$, (b) the good internal agreement among chemically equivalent bond lengths in the etu ligands, and (c) the close agreement between the ligand values found here and the recent, highly precise work of Vikane[31-33] on three-coordinate tellurium complexes containing etu. The average values of Vikane (followed immediately by the values found here) are: S−C, 1.721 (7), 1.712 (12); C(sp²)−N, 1.316 (12), 1.317 (18); N−C(sp³), 1.472 (14), 1.465 (11); C−C, 1.528 (7), 1.510 (9) Å.

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(10) The form of the isotropic temperature parameters is $\exp(-8\pi^2 U \sin^2\theta/\lambda^2)$.
(11) Following the suggestion of a referee, we have subsequently included an isotropic extinction correction in the refinement. The values of R_1 and R_2 decreased to 0.037 and 0.057, respectively. No positional parameter shifted by more than 0.7 times its esd. The Te thermal parameters changed by ~2.0 esd's. No bond length changed by more than 0.5 times its esd.
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The Crystal Structure of Prussian Blue: Fe$_4$[Fe(CN)$_6$]$_3$·xH$_2$O

H. J. BUSER,[1a] D. SCHWARZENBACH,[1b] W. PETTER,[1c] and A. LUDI*[1a]

Single crystals of Prussian Blue, Fe$_4$[Fe(CN)$_6$]$_3$·xH$_2$O (x = 14–16), have been grown by very slow diffusion of water vapor into a solution of Fe^{3+} and Fe(CN)$_6^{4-}$ in concentrated hydrochloric acid. The crystal structure of this compound has been investigated by x-ray diffraction studies of several single crystals from three different preparations. According to the density d_{exptl} = 1.75–1.81 g cm^{-3}, one unit of Fe$_4$[Fe(CN)6]$_3$·xH$_2$O is contained in the cubic primitive elementary cell with a = 10.166 Å, d_{calcd} = 1.78 g cm^{-3} for x = 15. The observation of non-face-centered reflections indicates a deviation from the well-known model for cubic polynuclear transition-metal cyanides in the space group $Fm3m$ (O_h^5). The Fe(CN)$_6$ positions are only partly occupied. Partial ordering of the corresponding vacancies, possibly related to the conditions for growing the crystals, causes the deviation from $Fm3m$ symmetry. The least-squares refinement in the space group O_h^1-$Pm3m$ for three different crystals gave R factors of 0.032, 0.042, and 0.046, respectively. The corresponding average distances are Fe(II)–C = 1.92 Å, C–N = 1.13 Å, and Fe(III)–N = 2.03 Å.

Introduction

The blue pigment called Prussian Blue can be considered as the first synthetic coordination compound.[2] Owing to its intense color, a property which is completely absent in the two constituent mononuclear complexes, Fe$_{aq}^{3+}$ and Fe(CN)$_6^{4-}$, it also found some analytical applications, e.g., spot tests in the classical analytical chemistry of iron and qualitative tests for nitrogen in organic compounds. Many investigations and speculations were concerned with the interpretation of the origin of this blue color and with the structure and bonding in Prussian Blue.[3] Very often Prussian Blue served as a test substance when new experimental techniques were developed[4,5] and when new theoretical concepts emerged. In particular, it represents the prototype of the mixed valence compounds,[6] a class of compounds which has attracted widespread interest during the last few years.

Depending on the specific conditions of the preparation, a wide variety of different names has been used for this polynuclear cyanide.[7] In particular, Prussian Blue and Turnbull's Blue were assumed to be two distinct compounds, namely iron(III) hexacyanoferrate(II) and iron(II) hexacyanoferrate(III), respectively. The results of various physical techniques, however, unambiguously demonstrated that the final product is always an iron(III) hexacyanoferrate(II) regardless of the combination of the starting complexes.[8] A further distinction was usually made between "soluble" and "insoluble" Prussian Blue. In this context the term "soluble" does not refer to a true solubility but only to the tendency of certain Prussian Blue samples to form colloidal solutions. This distinction has been related to the presence or absence of potassium, the formula KFeFe(CN)$_6$ representing the "soluble" and the formula Fe$_4$[Fe(CN)$_6$]$_3$ representing the "insoluble" form.[7,8]

Although numerous investigations were carried out with Prussian Blue, the details of its crystal structure and even the analytical composition were for a long time only partly resolved. The chemical literature (see ref 7–10 and references cited therein) reports the two formulas KFeFe(CN)$_6$ and/or