quickly revealed by structure factor, electron density calculations. Hydrogen atoms were located in later electron density maps. Their positions were not refined, and their temperature factors were constrained to $U = 0.076$ Å^2. Since the space group, $P2_12_12_1$, is a polar one, there are two possible enantiomeric forms, and the structure was therefore refined to convergence in each form. The full-matrix least-squares refinement with all nonhydrogen atoms anisotropic converged to weighted and unweighted R factors of 2.8% and 2.4%, respectively, for the enantiomeric form presented in the tables and figures. The corresponding R factors for the other enantiomeric form were as high as 4.1% and 3.7%, and we therefore concluded that the former was the correct one. In the final refinement cycle the largest shift was less than 1% of the associated estimated standard deviation, and the standard deviation of an observation of unit weight was 0.97. The largest peak in the subsequent difference electron density map was 0.32 e Å^{-3}.

Figure 1 shows a view of the *S*-(hydroxymethyl)thiosulfate anion, and Figure 2 is a projection of the cell contents down the *c* axis. Table I gives atomic coordinates, and Table II lists selected bond distances.

Discussion

Anions, $HOCH_2S_2O_3^-$, are arranged in head-to-tail spirals along 2_1 symmetry elements parallel to the (6.331 Å) *c* axis. The spirals are continuous because of intermolecular hydroxyl hydrogen to sulfonate oxygen hydrogen bonding (O(4)–H(19)···O(3)). There is also a continuous bond/hydrogen bond system in the *a* axis direction, involving –O(2)···H(1)–N(1)–Co–N(4)–H(15)···O(1)–S(1)– and repeated by the lattice translation. The shortest intramolecular sulfonate oxygen to hydroxyl oxygen contact is 3.22 Å for O(3)···O(4), which is considerably longer than the 2.86–2.88 Å for the three previously mentioned intermolecular contacts.

The $-S_2O_3$ fragment has the expected deviations from trigonal and mirror symmetries. The bond S(2)–C(5) is nearly trans to S(1)–O(1) and, in projection down the S(2)–S(1) bond, nearly bisects O(2)–S(1)–O(3). The dihedral angle O(1)–S(1)–S(2)–C(5) is 6° with C(5) closest to O(2) and with O(4) closest to O(3), which demonstrates the rotation of the $-SO_3$ group as a result of the position of O(4). O(1) is 0.07 Å closer to S(2) than are O(2) and O(3), which demonstrates the tilt of the O(1)–O(2)–O(3) plane away from C(5). Similar effects have been observed in the polythionates.[12,13]

The tetrabonded to dibonded S(1)–S(2) bond length of 2.078 (2) Å is perhaps short when compared to known polythionate tetrabonded to dibonded distances of range 2.09–2.13 Å.[12,13] The dibonded sulfur to carbon distance, S(2)–C(5), of 1.829 (5) Å is perhaps long when compared to bond lengths in $S_2(CH_3)_2$ (1.81 Å)[14] and $S_2(C_6H_5)_2$ (1.79 Å).[15] The C(5)–O(4) distance of 1.399 (6) Å is perhaps short compared to the corresponding distance in CH_3OH of 1.427 (7) Å.[16]

These distances are in accord with considerable ionic character in the S–C bond or with a loose complex between thiosulfate and protonated formaldehyde. They confirm the existence of "formaldehyde thiosulfate" and offer an explanation for the equilibria seen in solutions of formaldehyde and thiosulfate.

Acknowledgment. The authors express gratitude to Professor Olav Foss of this department for stimulating discussions and guidance. V.J. thanks the Royal Norwegian Ministry for Foreign Affairs for a Norwegian Government Scholarship.

Registry No. $[Co(en)_2Cl_2]O_3S_2CH_2OH$, 72709-18-3; $Na_2S_2O_3$, 7757-83-7; CH_2O, 50-00-0.

Supplementary Material Available: Listings of observed and calculated structure factors and of hydrogen atom positions (15 pages). Ordering information is given on any current masthead page.

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(12) Marøy, K. Doctoral Dissertation, University of Bergen, 1975.

(13) Foust, A. S.; Janickis, V.; Marøy, K. *Inorg. Chem.*, companion articles in this issue. Foust, A. S.; Janickis, V. *Ibid.*, companion note in this issue.

(14) Beagley, B.; McAloon, K. T. *Trans. Faraday Soc.* **1971**, *67*, 3216.

(15) Sacerdoti, M.; Gilli, G.; Domiano, P. *Acta Crystallogr., Sect. B* **1975**, *31*, 327.

(16) Venkatiswarlu, P.; Gordy, W. *J. Chem. Phys.* **1955**, *23*, 1200.

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Structures of Bis(μ-thiourea-*S*)-bis[bis(thiourea-*S*)tellurium(II)] Cations

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The structures of tris(ethylenethiourea-*S*)tellurium(II) perchlorate (I) and of two modifications of tris(trimethylenethiourea-*S*)tellurium(II) perchlorate (II and III) have been solved and refined with Mo Kα diffractometer data to reveal "planar", dimeric $L_2Te(\mu\text{-}L)_2TeL_2$ cations. The dimers are situated on crystallographic centers of symmetry and the Te_2S_6 moieties display approximate C_{2h} geometry with significant distortions from D_{2h} geometry along a B_{1g} vibrational coordinate. Trans pairs of Te–S bonds exhibit lengths in accord with three-center four-electron bonding. Crystals of I are monoclinic, of space group $P2_1/c$ with $a = 11.911$ (2) Å, $b = 11.455$ (2) Å, $c = 16.994$ (3) Å, $\beta = 112.10$ (2)°, and $Z = 2$ dimers. Crystals of II are triclinic, of space group $P\bar{1}$ with $a = 12.597$ (2) Å, $b = 10.018$ (3) Å, $c = 9.997$ (2) Å, $\alpha = 96.15$ (2)°, $\beta = 92.48$ (1)°, $\gamma = 77.89$ (1)°, and $Z = 1$ dimer. Crystals of III are monoclinic, of space group $P2_1/c$ with $a = 12.143$ (2) Å, $b = 14.675$ (3) Å, $c = 14.240$ (3) Å, $\beta = 106.49$ (2)°, and $Z = 2$ dimers. The Te–S distances range from 2.441 (2) to 3.040 (2) Å.

Introduction

Te(II), with four valence electrons and four two-electron-donor ligands, adopts a pseudooctahedral configuration with lone pairs of electrons above and below the coordination plane.[1] The ligands may be considered to contain two orthogonal three-center, four-electron bonding systems. Such systems may be very unsymmetrical when the opposing ligands are different in character. This "trans influence" in Te(II) complexes leads to bond-length variations which are much larger than those observed in the corresponding transition metal complexes.

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(1) Reviews of the chemistry and geometry of related examples of Te(II) and other linear three-center systems of the sixth main group have been presented by Foss, Vikane, and Hauge (see following references).

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for Hexakis(ethylenethiourea)ditellurium(II) Perchlorate[a]

atom	x	y	z	U_{11} (or U, Å^2)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Te	0.187 41 (5)	0.000 18 (5)	0.049 939 (32)	396 (3)	267 (3)	380 (3)	12 (3)	153 (2)	−21 (3)
S(1)	−0.005 05 (25)	0.034 51 (19)	0.116 27 (14)	717 (18)	338 (13)	369 (13)	15 (12)	281 (13)	15 (10)
C(11)	−0.004 9 (7)	0.181 2 (7)	0.123 3 (5)	350 (20)					
N(11)	0.001 7 (9)	0.261 7 (9)	0.069 1 (6)	827 (29)					
C(12)	−0.001 4 (8)	0.380 4 (8)	0.095 4 (6)	509 (25)					
C(13)	−0.005 1 (10)	0.366 5 (9)	0.182 2 (7)	656 (29)					
N(12)	−0.014 7 (10)	0.240 2 (9)	0.184 9 (6)	915 (32)					
S(2)	0.345 10 (24)	−0.018 37 (20)	−0.014 54 (19)	628 (17)	330 (15)	861 (19)	26 (12)	499 (15)	10 (12)
C(21)	0.359 4 (8)	−0.166 9 (8)	−0.022 1 (5)	406 (22)					
N(21)	0.356 0 (8)	−0.247 4 (7)	0.030 5 (5)	651 (24)					
C(22)	0.371 0 (9)	−0.363 0 (9)	0.002 7 (6)	601 (28)					
C(23)	0.391 0 (9)	−0.337 6 (10)	−0.078 6 (6)	659 (30)					
N(22)	0.389 3 (7)	−0.210 9 (7)	−0.082 6 (5)	559 (22)					
S(3)	0.336 81 (26)	0.024 99 (21)	0.201 31 (16)	707 (19)	399 (16)	476 (15)	73 (13)	−28 (14)	0 (11)
C(31)	0.352 2 (8)	0.172 2 (8)	0.213 1 (5)	422 (23)					
N(31)	0.352 1 (7)	0.251 4 (7)	0.157 1 (5)	529 (21)					
C(32)	0.364 6 (9)	0.371 0 (9)	0.190 8 (6)	561 (27)					
C(33)	0.372 9 (9)	0.349 5 (9)	0.281 7 (6)	611 (28)					
N(32)	0.369 4 (7)	0.223 1 (7)	0.287 2 (5)	543 (22)					
Cl(1)	0.215 55 (28)	0.176 11 (23)	0.427 58 (16)	845 (21)	448 (15)	437 (14)	−24 (15)	293 (15)	−4 (12)
O(11)	0.322 6 (10)	0.238 0 (10)	0.469 9 (6)	1346 (94)	1563 (101)	1184 (78)	−479 (77)	678 (74)	−45 (70)
O(12)	0.235 9 (14)	0.093 0 (7)	0.378 2 (6)	4927 (230)	493 (54)	1452 (87)	−63 (92)	2365 (127)	−100 (57)
O(13)	0.180 9 (8)	0.128 2 (8)	0.490 0 (5)	1383 (79)	1316 (80)	880 (61)	−485 (65)	782 (59)	−159 (54)
O(14)	0.141 3 (13)	0.264 1 (10)	0.381 2 (6)	2465 (146)	1444 (100)	984 (76)	1057 (100)	−18 (88)	157 (69)
Cl(2)	0.230 40 (30)	−0.180 00 (24)	−0.306 41 (16)	906 (23)	488 (16)	484 (16)	42 (16)	341 (16)	36 (13)
O(21)	0.228 4 (15)	−0.096 5 (7)	−0.252 5 (5)	5078 (243)	457 (51)	801 (63)	0 (96)	1415 (107)	−68 (48)
O(22)	0.166 1 (12)	−0.276 6 (8)	−0.295 8 (7)	2203 (123)	895 (72)	1871 (106)	−550 (77)	1418 (101)	−240 (69)
O(23)	0.188 8 (8)	−0.139 3 (7)	−0.390 3 (4)	1169 (69)	1240 (74)	530 (48)	286 (60)	262 (49)	252 (47)
O(24)	0.343 7 (9)	−0.224 3 (14)	−0.288 7 (7)	759 (73)	3551 (198)	1316 (93)	462 (95)	399 (68)	1320 (111)

[a] The form of the anisotropic thermal parameter is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + U_{23}klb^*c^*)/10000]$.

Foss[2] has pointed out that such asymmetric complexes may be considered as models for substitution processes at 2- and 3-coordinate Te(II), and they may also be considered as models for dissociation processes.

Te(II) also forms complexes, Te_2L_6, with two bridging and four terminal ligands in a planar arrangement.[1] The dimeric complexes may also be quite asymmetric in the solid state, generally with long tellurium to bridging-ligand distances. When dimeric complexes are considered, multicenter bonding models should replace three-center models. With distortions from D_{2h} geometry, there is loss in simplicity of interpretation of the molecular orbitals. The distortions of the dimers are consistent with three-center bonding models and clearly display incipient dissociation along one or a combination of two of the vibrational coordinates.

The structures of several Te(II) and Se(II) dimeric complexes with halide and pseudohalide bridges are known,[1] but, to date, only one dimer with thiourea bridges has been examined crystallographically.[6] We report here the structures of three hexakis(substituted thiourea)ditellurium(II) perchlorate salts and discuss the bonding and incipient dissociation models for the series.

Experimental Section

Crystalline samples of the three compounds were kindly supplied by Professor Olav Foss of this department. Preparation of the compounds is described in ref 7 and 8, where the space groups were first reported.

All compounds were subjected to preliminary film examination and then mounted on a Siemens off-line automatic quarter-circle single-crystal diffractometer equipped with a Mo X-ray source and Nb filter, scintillation counter, and pulse-height discriminator. Several reflections were carefully centered in θ, ϕ, and χ for the derivation of orientation and preliminary lattice parameters. Data were collected in one independent unit to a maximum θ of 25° with the "*five-value*" procedure, a symmetric scan of 0.8° θ, and a maximum scan time of 24 s/deg θ. Four standard reflections were measured after every 50 data reflections. Finally 20 reasonably intense reflections over 20° θ were carefully centered in θ and ω for the derivation of accurate lattice parameters. Data were corrected[9] for Lorentz and polarization effects, and weights were assigned according to standard formulas[10] for counting statistics and instrument instability. Reflections more than three standard deviations above background were used in the subsequent calculations which were performed on a Univac 1110 computer.

The structures were solved by Patterson–Fourier calculations and refined by weighted full-matrix least-squares calculations. Atoms lighter than oxygen were, with the exceptions noted, refined isotropically while O, Cl, S, and Te were refined anisotropically. Anomalous dispersion was included for S and Te, and extinction effects were judged unimportant. Hydrogen atoms were, with exceptions noted, placed in assumed positions and not refined. In each case the independent unit is half of a dimer, and the dimers are centrosymmetric.

Hexakis(ethylenethiourea-*S*)ditellurium(II) perchlorate[7] occurs as yellow plates, (100), also bounded by (001) and (011). Crystals are nearly always twinned along (100), giving a pseudo mirror plane normal to the plate face. The data crystal, an untwinned individual, was an approximately hexagonal plate 0.15 mm thick with 0.25 mm between the remaining parallel faces. It was mounted on a glass fiber nearly parallel to [011]. The crystals are monoclinic, of space group $P2_1/c$ with $a = 11.911$ (2) Å, $b = 11.455$ (2) Å, $c = 16.994$ (3) Å, $\beta = 112.10$ (2)°, $V = 2148$ Å^3, mol wt 1266, D(obsd) = 1.93 g cm^{-3}, and D(calcd for $Z = 2$ dimers) = 1.96 g cm^{-3}. A systematic weakness of reflections with $k + l$ odd implies that the Te atoms must occupy general positions with either x and y or z nearly zero. There were 4171 reflections measured, of which 1286 were less than three standard deviations above background. The instrument instability was 1.5%. The refinement converged to weighted and unweighted R factors of

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(2) Foss, O. *Sel. Top. Struct. Chem.* **1967**, 145.
(3) Foss, O. *Pure Appl. Chem.* **1970**, *24*, 31.
(4) Vikane, O. Doctoral Thesis, University of Bergen, 1975.
(5) Hauge, S. Doctoral Thesis, University of Bergen, 1977.
(6) Foss, O.; Hauge, S. *Acta Chem. Scand.* **1965**, *19*, 2395.
(7) Foss, O.; Fossen, S. *Acta Chem. Scand.* **1961**, *15*, 1620.
(8) Foss, O.; Marøy, K. *Acta Chem. Scand.* **1961**, *15*, 1947.
(9) "The X-Ray System—Version of June 1972" (Technical Report TR-192 of the Computer Science Center, University of Maryland, June 1972) and other locally written programs.
(10) Busing, W. R.; Levy, H. A. *J. Chem. Phys.* **1957**, *26*, 563.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for Triclinic Hexakis(trimethylenethiourea)ditellurium(II) Perchlorate[a]

atom	*x*	*y*	*z*	U_{11} (or *U*, Å^2)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Te	0.133 410 (33)	0.091 75 (4)	−0.046 08 (4)	445 (2)	338 (2)	308 (2)	−66 (2)	28 (2)	−8 (1)
S(1)	0.073 15 (13)	−0.077 99 (14)	0.162 17 (14)	493 (9)	349 (8)	345 (7)	−67 (7)	−35 (7)	53 (6)
C(11)	0.137 7 (5)	−0.248 5 (6)	0.147 2 (5)	387 (13)					
N(11)	0.149 6 (4)	−0.315 1 (5)	0.255 4 (5)	462 (12)					
C(12)	0.197 6 (6)	−0.461 8 (8)	0.255 9 (7)	647 (19)					
C(13)	0.193 3 (7)	−0.530 2 (9)	0.120 0 (9)	826 (24)					
C(14)	0.230 4 (7)	−0.457 5 (8)	0.016 2 (8)	748 (22)					
N(12)	0.174 2 (4)	−0.311 5 (5)	0.030 4 (5)	518 (13)					
S(2)	0.137 23 (15)	0.272 20 (15)	−0.190 58 (15)	691 (11)	357 (8)	420 (8)	−158 (8)	82 (8)	34 (6)
C(21)	0.173 1 (5)	0.191 7 (6)	−0.350 5 (5)	391 (13)					
N(21)	0.174 7 (4)	0.062 4 (5)	−0.385 7 (5)	467 (12)					
C(22)	0.201 5 (6)	−0.002 1 (7)	−0.521 6 (7)	618 (18)					
C(23)	0.276 1 (6)	0.070 8 (8)	−0.581 5 (7)	648 (19)					
C(24)	0.231 0 (6)	0.222 1 (8)	−0.572 5 (8)	678 (20)					
N(22)	0.198 7 (4)	0.272 4 (5)	−0.434 3 (5)	529 (13)					
S(3)	0.330 48 (15)	0.067 05 (19)	0.033 33 (18)	496 (10)	651 (11)	528 (10)	−151 (9)	−97 (8)	−87 (8)
C(31)	0.383 8 (5)	−0.070 0 (6)	−0.084 2 (6)	457 (14)					
N(31)	0.397 8 (5)	−0.194 4 (6)	−0.049 8 (5)	564 (14)					
C(32)	0.445 1 (7)	−0.317 0 (9)	−0.140 1 (9)	796 (23)					
C(33)	0.484 7 (10)	−0.284 4 (13)	−0.258 1 (12)	1242 (38)					
C(34)	0.450 2 (7)	−0.156 4 (9)	−0.307 7 (9)	806 (24)					
N(32)	0.407 6 (5)	−0.046 9 (6)	−0.203 7 (6)	581 (14)					
Cl(1)	−0.107 17 (16)	0.310 43 (17)	0.351 49 (16)	738 (12)	490 (9)	469 (9)	−117 (9)	−9 (8)	62 (7)
O(11)	−0.058 9 (6)	0.240 8 (7)	0.461 0 (6)	1107 (51)	1240 (52)	691 (36)	−28 (42)	−29 (35)	387 (36)
O(12)	−0.154 1 (7)	0.220 2 (6)	0.261 8 (6)	1875 (77)	811 (42)	850 (43)	−442 (47)	−353 (47)	−67 (34)
O(13)	−0.029 4 (7)	0.354 0 (10)	0.283 1 (9)	1362 (72)	2379 (106)	1637 (78)	−835 (74)	49 (60)	1120 (77)
O(14)	−0.1873 (8)	0.421 8 (7)	0.395 1 (8)	1720 (81)	786 (46)	1530 (68)	279 (50)	71 (60)	−232 (45)
Cl(2)	0.496 56 (17)	0.285 96 (17)	−0.288 21 (17)	850 (14)	479 (9)	516 (10)	−151 (9)	22 (9)	39 (8)
O(21)	0.481 9 (11)	0.373 5 (9)	−0.385 6 (8)	3909 (169)	1135 (61)	1122 (60)	−824 (84)	−439 (84)	644 (52)
O(22)	0.474 5 (8)	0.163 4 (7)	−0.343 5 (7)	1986 (85)	887 (48)	1240 (57)	−680 (53)	−179 (56)	−40 (42)
O(23)	0.425 8 (9)	0.336 5 (12)	−0.185 9 (9)	1864 (99)	2563 (122)	1142 (64)	358 (86)	731 (66)	−118 (71)
O(24)	0.597 6 (7)	0.268 9 (12)	−0.228 8 (8)	1299 (71)	3334 (139)	1129 (60)	−1339 (86)	−396 (54)	764 (75)

[a] The form of the anisotropic thermal parameter is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + U_{23}klb^*c^*)/10000]$.

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for Monoclinic Hexakis(trimethylenethiourea)ditellurium(II) Perchlorate[a]

atom	*x*	*y*	*z*	U_{11} (or *U*, Å^2)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Te	0.153 76 (5)	0.069 47 (4)	0.020 51 (4)	453 (4)	357 (3)	362 (3)	5 (3)	127 (2)	62 (3)
S(1)	−0.055 76 (19)	0.107 86 (15)	0.060 30 (16)	551 (13)	381 (11)	444 (12)	60 (9)	145 (9)	44 (9)
C(11)	−0.103 5 (7)	0.184 9 (6)	−0.034 5 (6)	434 (19)					
N(11)	−0.092 8 (7)	0.271 8 (6)	−0.013 1 (6)	554 (19)					
C(12)	−0.130 4 (9)	0.344 9 (8)	−0.086 3 (8)	663 (26)					
C(13)	−0.129 9 (10)	0.308 7 (9)	−0.185 0 (9)	766 (31)					
C(14)	−0.192 7 (10)	0.221 1 (9)	−0.208 3 (9)	780 (32)					
N(12)	−0.151 7 (7)	0.160 0 (6)	−0.124 6 (6)	591 (20)					
S(2)	0.337 87 (21)	0.028 11 (17)	−0.021 33 (18)	510 (13)	606 (13)	478 (12)	38 (11)	211 (10)	−24 (12)
C(21)	0.427 0 (7)	0.008 0 (6)	0.097 2 (6)	452 (20)					
N(21)	0.482 0 (7)	0.075 4 (6)	0.148 4 (6)	596 (19)					
C(22)	0.564 1 (10)	0.062 9 (9)	0.245 8 (9)	779 (31)					
C(23)	0.534 6 (11)	−0.019 7 (10)	0.294 4 (11)	894 (37)					
C(24)	0.516 4 (11)	−0.099 7 (9)	0.226 3 (10)	782 (32)					
N(22)	0.437 0 (6)	−0.075 8 (6)	0.130 7 (6)	569 (18)					
S(3)	0.231 00 (21)	0.219 28 (15)	0.092 34 (15)	751 (16)	398 (11)	344 (11)	−87 (10)	191 (10)	7 (9)
C(31)	0.226 3 (7)	0.291 3 (6)	−0.005 6 (6)	400 (18)					
N(31)	0.250 3 (9)	0.261 6 (8)	−0.083 8 (9)	912 (31)					
C(32)	0.248 3 (22)	0.321 5 (13)	−0.168 1 (9)	3196 (265)	1179 (140)	364 (65)	−999 (157)	744 (108)	−81 (74)
C(33)	0.254 1 (24)	0.413 5 (13)	−0.140 9 (17)	2790 (268)	914 (133)	1706 (189)	557 (147)	1631 (204)	724 (132)
C(34)	0.210 4 (15)	0.447 8 (8)	−0.068 0 (11)	1694 (137)	401 (66)	907 (96)	−100 (67)	390 (94)	267 (60)
N(32)	0.207 1 (8)	0.376 9 (6)	0.004 7 (7)	672 (23)					
Cl(1)	0.071 90 (21)	0.414 30 (15)	0.214 71 (16)	711 (15)	426 (13)	428 (11)	55 (10)	155 (10)	−7 (9)
O(11)	0.009 2 (9)	0.471 7 (7)	0.259 9 (6)	1437 (78)	956 (66)	593 (48)	489 (59)	255 (48)	−120 (45)
O(12)	0.056 2 (11)	0.438 7 (7)	0.117 2 (6)	1833 (96)	1021 (74)	551 (48)	559 (69)	450 (54)	147 (48)
O(13)	0.187 6 (9)	0.412 1 (10)	0.267 1 (10)	795 (64)	1795 (130)	1390 (101)	2 (71)	90 (62)	−335 (94)
O(14)	0.031 3 (10)	0.324 8 (7)	0.214 2 (9)	1469 (88)	705 (62)	1576 (102)	−149 (56)	833 (78)	−13 (64)
Cl(2)	0.587 76 (24)	0.290 51 (19)	0.024 14 (21)	749 (17)	633 (16)	653 (16)	−84 (13)	225 (13)	−15 (13)
O(21)	0.520 2 (14)	0.263 6 (9)	0.080 8 (11)	2195 (136)	1192 (96)	1642 (118)	−784 (94)	1239 (112)	−362 (86)
O(22)	0.649 2 (24)	0.362 4 (12)	0.053 5 (17)	4499 (340)	1400 (136)	2516 (211)	−1828 (190)	2119 (237)	−838 (145)
O(23)	0.550 7 (21)	0.273 2 (12)	−0.072 1 (10)	3864 (265)	1567 (140)	821 (84)	−823 (160)	547 (122)	−287 (89)
O(24)	0.669 4 (13)	0.219 8 (15)	0.045 0 (17)	1318 (113)	2230 (202)	2759 (231)	368 (115)	277 (125)	−366 (174)

[a] The form of the anisotropic thermal parameter is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + U_{23}klb^*c^*)/10000]$.

5.8% and 5.3%, and the standard deviation of an observation of unit weight was 3.9. The largest peak in the final difference electron density map was 1.57 e Å^{-3}, and the largest shift in the final refinement cycle was 21% of the associated standard deviation.

Triclinic hexakis(trimethylenethiourea-*S*)ditellurium(II) perchlorate[8] occurs as yellow plates, (110), also bounded by $(1\bar{1}0)$ and

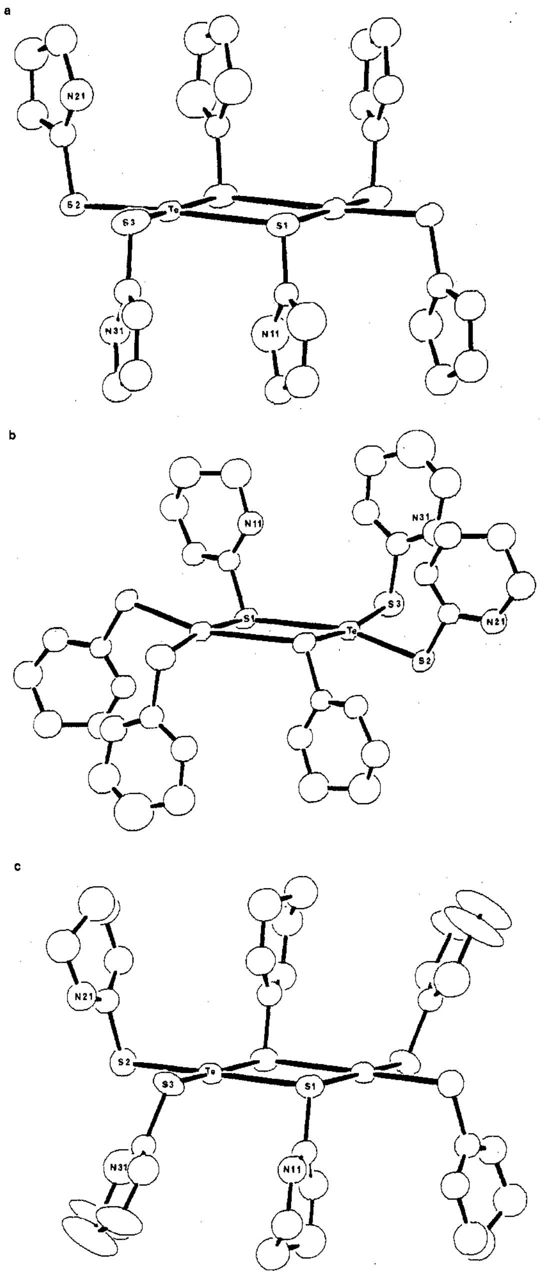

Figure 1. Perspective views of the dimeric cations of (a) hexakis(ethylenethiourea)ditellurium(II) perchlorate and (b) the triclinic form and (c) the monoclinic form of hexakis(trimethylenethiourea)ditellurium(II) perchlorate. Thermal ellipsoids are at 50% probability.

(001). The data crystal was 0.13 mm thick with 0.24 and 0.25 mm, respectively, between the remaining parallel faces and was mounted on a glass fiber nearly parallel to [120]. The space group is $P\bar{1}$ with $a = 12.597$ (2) Å, $b = 10.018$ (3) Å, $c = 9.997$ (2) Å, $\alpha = 96.15$ (2)°, $\beta = 92.48$ (1)°, $\gamma = 77.89$ (1)°, $V = 1226$ Å^3, mol wt 1350, D(obsd) = 1.82 g cm^{-3}, and D(calcd for $Z = 1$ dimer) = 1.83 g cm^{-3}. There were 4294 reflections measured, of which 487 were less than three standard deviations above background. The instrument instability was 1.2%. The refinement converged to weighted and unweighted R factors of 5.1% and 4.5%, and the standard deviation of an observation of unit weight was 4.2. The largest peak in the final difference electron density map was 1.2 e Å^{-3}, and the largest shift in the final refinement cycle was 3% of the associated standard deviation.

Table IV. Bond Distances (Å) and Angles (Deg) for Hexakis(ethylenethiourea)ditellurium(II) Perchlorate

	(a) Bond Distances		
Te–S(1)	2.9281 (32)	Te–S(2)	2.507 (4)
Te–S(1)′	2.8599 (21)	Te–S(3)	2.5250 (23)
C(11)–S(1)	1.679 (8)	N(11)–C(12)	1.433 (14)
C(11)–N(11)	1.323 (14)	C(12)–C(13)	1.495 (16)
C(11)–N(12)	1.284 (15)	C(13)–N(12)	1.448 (15)
C(21)–S(2)	1.715 (9)	N(21)–C(22)	1.436 (14)
C(21)–N(21)	1.292 (13)	C(22)–C(23)	1.513 (17)
C(21)–N(22)	1.304 (14)	C(23)–N(22)	1.449 (14)
C(31)–S(3)	1.695 (9)	N(31)–C(32)	1.466 (13)
C(31)–N(31)	1.310 (12)	C(32)–C(33)	1.526 (15)
C(31)–N(32)	1.328 (12)	C(33)–N(32)	1.449 (13)
Cl(1)–O(11)	1.394 (11)	Cl(1)–O(13)	1.384 (11)
Cl(1)–O(12)	1.346 (12)	Cl(1)–O(14)	1.372 (12)
Cl(2)–O(21)	1.327 (10)	Cl(2)–O(23)	1.397 (8)
Cl(2)–O(22)	1.391 (12)	Cl(2)–O(24)	1.360 (12)
	(b) Bond Angles		
S(1)–Te–S(2)	175.97 (7)	S(2)–Te–S(1)′	88.39 (9)
S(1)–Te–S(3)	86.92 (9)	S(3)–Te–S(1)′	175.59 (10)
S(1)–Te–S(1)′	89.18 (8)	Te–S(1)–Te′	90.82 (8)
S(2)–Te–S(3)	95.62 (10)		
C(11)–S(1)–Te	100.4 (4)	C(11)–N(11)–C(12)	115.2 (10)
C(11)–S(1)–Te′	100.87 (25)	N(11)–C(12)–C(13)	102.7 (8)
N(11)–C(11)–S(1)	130.0 (8)	C(12)–C(13)–N(12)	99.8 (9)
N(12)–C(11)–S(1)	125.7 (8)	C(11)–N(12)–C(13)	117.7 (11)
N(11)–C(11)–N(12)	104.3 (9)		
C(21)–S(2)–Te	103.2 (4)	C(21)–N(21)–C(22)	112.8 (9)
N(21)–C(21)–S(2)	128.5 (8)	N(21)–C(22)–C(23)	101.8 (9)
N(22)–C(21)–S(2)	120.3 (8)	C(22)–C(23)–N(22)	103.3 (9)
N(21)–C(21)–N(22)	110.9 (9)	C(21)–N(22)–C(23)	110.6 (9)
C(31)–S(3)–Te	103.53 (27)	C(31)–N(31)–C(32)	112.9 (8)
N(31)–C(31)–S(3)	129.0 (7)	N(31)–C(32)–C(33)	101.7 (8)
N(32)–C(31)–S(3)	121.1 (7)	C(32)–C(33)–N(32)	103.4 (8)
N(31)–C(31)–N(32)	109.9 (8)	C(31)–N(32)–C(33)	112.0 (8)
O(11)–Cl(1)–C(12)	109.6 (9)	O(12)–Cl(1)–O(13)	111.7 (7)
O(11)–Cl(1)–O(13)	106.5 (6)	O(12)–Cl(1)–O(14)	112.8 (6)
O(11)–Cl(1)–O(14)	100.9 (7)	O(13)–Cl(1)–O(14)	114.5 (8)
O(21)–Cl(2)–O(22)	109.2 (9)	O(22)–Cl(2)–O(23)	113.2 (6)
O(21)–Cl(2)–O(23)	111.8 (5)	O(22)–Cl(2)–O(24)	102.8 (8)
O(21)–Cl(2)–O(24)	112.8 (9)	O(23)–Cl(2)–O(24)	106.8 (7)

Monoclinic hexakis(trimethylenethiourea-*S*)ditellurium(II) perchlorate[8] occurs as yellow prisms elongated along [100] and bounded by (011) and (01$\bar{1}$). The data crystal was 0.27 mm long with 0.20 mm between the remaining parallel faces and was mounted on a glass fiber nearly parallel to [100]. The space group is $P2_1/c$ with $a = 12.143$ (2) Å, $b = 14.675$ (3) Å, $c = 14.240$ (3) Å, $\beta = 106.49$ (2)°, $V = 2433$ Å^3, mol wt 1350, D(obsd) = 1.82 g cm^{-3}, and D(calcd for $Z = 2$ dimers) = 1.84 g cm^{-3}. There were 4679 reflections measured, of which 1472 were less than three standard deviations above background. The instrument instability was 3.9%. The trimethylene fragment of one of the terminal thioureas is clearly disordered. Examination of a difference Fourier synthesis suggested a model with three anisotropic carbon atoms, while refinement stability and chemical sense suggested exclusion of the attached hydrogen atoms. The refinement of this model converged to weighted and unweighted R factors of 5.9% and 5.0%, and the standard deviation of an observation of unit weight was 1.5. The largest peak in the final difference electron density map was 1.36 e Å^{-3}, and the largest shift in the final refinement cycle was 27% of the associated standard deviation.

Description of the Structures

As illustrated in Figure 1, the cations are all of the type $L_2Te(\mu\text{-}L)_2TeL_2$. The Te_2S_6 portions of the dimers are distinctly not of D_{2h} symmetry but rather approach C_{2h} symmetry. Since the thiourea C and N atoms are distinctly out of the Te_2S_6 plane, the cations possess only the crystallographically required C_i site symmetry.

With three crystallographic independent ligands, there are four possible isomers, of which two are illustrated. Forgetting for the moment the bridging ligands, the two isomers observed are reminiscent of the cis and trans forms of the telluropentathionate dianion.[11-13] The two missing isomers are those

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(11) Marøy, K. *Acta Chem. Scand.* **1973**, *27*, 1695.
(12) Marøy, K. *Acta Chem. Scand.* **1971**, *25*, 2557.
(13) Gjerrestad, K.; Marøy, K. *Acta Chem. Scand.* **1973**, *27*, 1653.

Table V. Bond Distances (Å) and Angles (Deg) for the Triclinic Form of Hexakis(trimethylenethiourea)ditellurium(II) Perchlorate

(a) Bond Distances

Te–S(1)	3.0395 (17)	Te–S(2)	2.4411 (18)
Te–S(1)′	2.8270 (17)	Te–S(3)	2.5434 (19)
C(11)–S(1)	1.725 (5)	C(12)–C(13)	1.459 (11)
C(11)–N(11)	1.317 (8)	C(13)–C(14)	1.474 (13)
C(11)–N(12)	1.319 (7)	C(14)–N(12)	1.480 (9)
N(11)–C(12)	1.468 (9)		
C(21)–S(2)	1.744 (6)	C(22)–C(23)	1.485 (12)
C(21)–N(21)	1.302 (8)	C(23)–C(24)	1.497 (10)
C(21)–N(22)	1.318 (8)	C(24)–N(22)	1.464 (9)
N(21)–C(22)	1.461 (8)		
C(31)–S(3)	1.747 (6)	C(32)–C(33)	1.396 (16)
C(31)–N(31)	1.302 (9)	C(33)–C(34)	1.401 (15)
C(31)–N(32)	1.301 (9)	C(34)–N(32)	1.459 (10)
N(31)–C(32)	1.476 (9)		
Cl(1)–O(11)	1.408 (6)	Cl(2)–O(21)	1.360 (9)
Cl(1)–O(12)	1.405 (7)	Cl(2)–O(22)	1.369 (8)
Cl(1)–O(13)	1.385 (10)	Cl(2)–O(23)	1.370 (10)
Cl(1)–O(14)	1.383 (7)	Cl(2)–O(24)	1.366 (9)

(b) Bond Angles

S(1)–Te–S(2)	164.24 (5)	S(2)–Te–S(1)′	87.03 (6)
S(1)–Te–S(3)	94.86 (6)	S(3)–Te–S(1)′	170.39 (5)
S(1)–Te–S(1)′	84.94 (4)	Te–S(1)–Te′	95.06 (4)
S(2)–Te–S(3)	95.31 (7)		
Te–S(1)–C(11)	115.22 (21)	C(11)–N(11)–C(12)	124.2 (5)
Te′–S(1)–C(11)	101.71 (21)	N(11)–C(12)–C(13)	109.6 (6)
S(1)–C(11)–N(11)	118.4 (4)	C(12)–C(13)–C(14)	113.7 (8)
S(1)–C(11)–N(12)	121.1 (5)	C(13)–C(14)–N(12)	109.8 (6)
N(11)–C(11)–N(12)	120.5 (5)	C(11)–N(12)–C(14)	121.7 (6)
Te–S(2)–C(21)	107.11 (21)	N(21)–C(22)–C(23)	109.2 (6)
S(2)–C(21)–N(21)	123.3 (5)	C(22)–C(23)–C(24)	111.2 (6)
S(2)–C(21)–N(22)	114.7 (4)	C(23)–C(24)–N(22)	109.6 (6)
N(21)–C(21)–N(22)	122.0 (5)	C(21)–N(22)–C(24)	122.1 (6)
C(21)–N(21)–C(22)	122.5 (6)		
Te–S(3)–C(31)	96.62 (22)	N(31)–C(32)–C(33)	112.8 (8)
S(3)–C(31)–N(31)	118.7 (5)	C(32)–C(33)–C(34)	122.8 (9)
S(3)–C(31)–N(32)	120.0 (5)	C(33)–C(34)–N(32)	113.1 (8)
N(31)–C(31)–N(32)	121.3 (5)	C(31)–N(32)–C(34)	122.9 (6)
C(31)–N(31)–C(32)	123.0 (6)		
O(11)–Cl(1)–O(12)	109.1 (4)	O(12)–Cl(1)–O(13)	108.1 (5)
O(11)–Cl(1)–O(13)	110.3 (5)	O(12)–Cl(1)–O(14)	108.8 (5)
O(11)–Cl(1)–O(14)	110.7 (4)	O(13)–Cl(1)–O(14)	109.8 (5)
O(21)–Cl(2)–O(22)	108.2 (5)	O(22)–Cl(2)–O(23)	108.1 (7)
O(21)–Cl(2)–O(23)	110.2 (6)	O(22)–Cl(2)–O(24)	111.4 (6)
O(21)–Cl(2)–O(24)	113.4 (8)	O(23)–Cl(2)–O(24)	105.3 (6)

Table VI. Bond Distances (Å) and Angles (Deg) for the Monoclinic Form of Hexakis(trimethylenethiourea)ditellurium(II) Perchlorate

(a) Bond Distances

Te–S(1)	2.8160 (26)	Te–S(2)	2.5452 (28)
Te–S(1)′	2.9556 (22)	Te–S(3)	2.4929 (22)
C(11)–S(1)	1.730 (8)	C(12)–C(13)	1.504 (18)
C(11)–N(11)	1.309 (12)	C(13)–C(14)	1.483 (18)
C(11)–N(12)	1.302 (11)	C(14)–N(12)	1.461 (15)
N(11)–C(12)	1.475 (14)		
C(21)–S(2)	1.752 (8)	C(22)–C(23)	1.488 (21)
C(21)–N(21)	1.297 (12)	C(23)–C(24)	1.500 (20)
C(21)–N(22)	1.312 (12)	C(24)–N(22)	1.470 (14)
N(21)–C(22)	1.472 (13)		
C(31)–S(3)	1.738 (9)	C(32)–C(33)	1.400 (28)
C(31)–N(31)	1.304 (16)	C(33)–C(34)	1.388 (33)
C(31)–N(32)	1.293 (13)	C(34)–N(32)	1.476 (17)
N(31)–C(32)	1.483 (21)		
Cl(1)–O(11)	1.408 (11)	Cl(2)–O(21)	1.362 (18)
Cl(1)–O(12)	1.394 (9)	Cl(2)–O(22)	1.291 (21)
Cl(1)–O(13)	1.392 (10)	Cl(2)–O(23)	1.339 (14)
Cl(1)–O(14)	1.402 (11)	Cl(2)–O(24)	1.407 (19)

(b) Bond Angles

S(1)–Te–S(2)	177.01 (7)	S(2)–Te–S(1)′	88.98 (8)
S(1)–Te–S(3)	89.84 (8)	S(3)–Te–S(1)′	177.82 (9)
S(1)–Te–S(1)′	88.14 (7)	Te–S(1)–Te′	91.86 (7)
S(2)–Te–S(3)	93.05 (8)		
Te–S(1)–C(11)	95.49 (33)	C(11)–N(11)–C(12)	123.6 (8)
Te′–S(1)–C(11)	105.25 (28)	N(11)–C(12)–C(13)	108.7 (9)
S(1)–C(11)–N(11)	117.7 (6)	C(12)–C(13)–C(14)	112.2 (12)
S(1)–C(11)–N(12)	122.8 (7)	C(13)–C(14)–N(12)	108.3 (9)
N(11)–C(11)–N(12)	119.4 (8)	C(11)–N(12)–C(14)	125.8 (9)
Te–S(2)–C(21)	99.13 (34)	N(21)–C(22)–C(23)	110.6 (10)
S(2)–C(21)–N(21)	119.5 (7)	C(22)–C(23)–C(24)	110.3 (13)
S(2)–C(21)–N(22)	118.4 (6)	C(23)–C(24)–N(22)	110.5 (10)
N(21)–C(21)–N(22)	122.1 (8)	C(21)–N(22)–C(24)	121.9 (8)
C(21)–N(21)–C(22)	122.5 (9)		
Te–S(3)–C(31)	106.53 (27)	N(31)–C(32)–C(33)	111.1 (15)
S(3)–C(31)–N(31)	121.1 (8)	C(32)–C(33)–C(34)	123.8 (22)
S(3)–C(31)–N(32)	117.8 (7)	C(33)–C(34)–N(32)	111.2 (12)
N(31)–C(31)–N(32)	120.9 (10)	C(31)–N(32)–C(34)	124.3 (10)
C(31)–N(31)–C(32)	122.5 (12)		
O(11)–Cl(1)–O(12)	111.2 (6)	O(12)–Cl(1)–O(13)	111.8 (8)
O(11)–Cl(1)–O(13)	111.4 (7)	O(12)–Cl(1)–O(14)	106.7 (7)
O(11)–Cl(1)–O(14)	109.2 (7)	O(13)–Cl(1)–O(14)	106.3 (8)
O(24)–Cl(2)–O(21)	99.7 (11)	O(21)–Cl(2)–O(22)	115.8 (14)
O(24)–Cl(2)–O(22)	103.1 (13)	O(21)–Cl(2)–O(23)	117.8 (12)
O(24)–Cl(2)–O(23)	95.0 (13)	O(22)–Cl(2)–O(23)	118.8 (14)

in which two trans sulfur atoms on a given tellurium have the shorter Te–S distance and a syn-periplanar conformation of the S–C bonds.

The Te–S distances range from 2.441 (2) to 3.040 (2) Å, and, significantly, the extreme bond lengths are trans to each other in the same molecule. Terminal Te–S bonds are less than 2.55 Å, and bridging Te–S distances are greater than 2.81 Å. In a given cation there is one bridge bond 2.81–2.86 Å, and the other bridge bond is 2.92–3.04 Å and is trans to the shorter terminal Te–S bond.

The SC(NC)$_2$ portions of the thiourea ligands are essentially planar, as is characteristic of the isolated thiourea molecules.[14] The perchlorate anions form a network of hydrogen bonds with the amine hydrogens of the thiourea ligands.

Discussion

One might consider Te$_2$L$_6$ complexes to possess two σ orbitals for each Te(II) and for each bridging ligand and one σ orbital for each terminal ligand. In D_{2h} symmetry, these orbitals span 3 A$_{1g}$ + 3 B$_{2u}$ + 3 B$_{3u}$ + 3 B$_{1g}$ and the Te–S bond stretching vibrations span 2 A$_{1g}$ + 2 B$_{2u}$ + 2 B$_{3u}$ + 2 B$_{1g}$. As with isolated 3c–4e systems, we take the molecular orbitals to be a filled bonding set, a filled nonbonding set, and an empty antibonding set, where each set might be taken to be A$_{1g}$ + B$_{2u}$ + B$_{3u}$ + B$_{1g}$. The extreme distortions from D_{2h} symmetry and the problems of configuration interaction make us hesitant to press the molecular orbital model. We can, however, apply "localized bonding" models to the structures with some success.

Vikane,[4] for example, has demonstrated that the Pauling relationship[15] between bond length and bond order may be applied very consistently to the three-center four-electron bonding of a wide variety of monomeric Te(II) complexes. That is, with the assumption that there is one full bond for a pair of trans ligands held by three-center four-electron bonding, Vikane derived the covalent radii for Te(II) of 1.34 Å for two-center two-electron bonding and 1.67 Å for three-center four-electron bonding. A dimeric complex with multicenter bonding would not require pairwise correlation of bond lengths, but, nevertheless, with Vikane's relationship, our six trans pairs of Te–S bonds have bond orders 1.00–1.02 except

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(14) Wheatley, P. J. *Acta Crystallogr.* **1953**, *6*, 369.

(15) Pauling, L. *J. Am. Chem. Soc.* **1947**, *69*, 542. Bond length/bond order rules have been successfully applied to borates and elicited a noteworthy comment from Professor C. A. Coulson (cited on p 1424 of ref 16).

(16) Donnay, G.; Donnay, J. D. H. *Acta Crystallogr., Sect. B* **1973**, *29*, 1417.

for the one longest pair where the bond order is 1.06.

Thiourea contains a planar 3-coordinate carbon atom. That carbon atom is connected to two planar 3-coordinate nitrogen atoms and a sulfur atom. The SCN_2 fragment thus has six electrons in four π-symmetry orbitals. The π bonding may be highly delocalized although it has been estimated that for ethylenethiourea the resonance structure with a single bond to sulfur contributes approximately 80%.[14]

On complexation to Te(II) the thioureas should display even less C–S π bonding because this is a means to delocalize the positive charge on Te to the N atoms. Loss of electron density from the sulfur in such a process would imply a smaller sulfur atom and decreased C–S bond length while the loss of C–S π bonding implies increased C–S bond length. For the bridging thioureas the C–S bonds are relatively short and there seems no significant difference in the C–N bond lengths between terminal and bridging ligands.

A vibrational analysis of the Te_2S_6 core indicates the possible unimolecular dissociation modes available to the complex. For simplicity we consider the vibrations of hypothetical D_{2h} complexes. We further focus attention on the four modes, $A_{1g} + B_{2u} + B_{3u} + B_{1g}$, that could separate the dimers at the bridge bonds because it is the bridge bonds which are long and weak.

The A_{1g} and B_{2u} modes carried to dissociation lead to 2-coordinate Te(II) species and therefore seem unlikely. Complexes of Te(II) tend to be 4-coordinate except in those cases where the trans influence and electrostatic effects mitigate.

The B_{1g} vibration carried to dissociation preserves centrosymmetry, while separating a dimer into two T-shaped, 3-coordinate complexes. This is the distortion from D_{2h} symmetry of the four known hexakis(thiourea-*S*)ditellurium(II) cations. The products resulting from a complete separation along the B_{1g} coordinate, T-shaped Te(II) complexes, have precedent in the $C_6H_5TeL_2$ complexes where the extreme trans influence of the phenyl group essentially precludes a ligand trans to phenyl.[17]

The B_{3u} vibration lengthens both bonds to one bridge ligand and would lead to expulsion of one bridge ligand and retention of the other. The products here are two T-shaped Te(II) complexes linked by a bridging ligand. There is one example[18] of two 4-coordinate Te(II) complexes linked by a single bridge, and the B_{3u} distortion is seen in the monoclinic form of di-μ-bromo-bis[bis(ethylenethiourea-*S*)tellurium(II)] bromide.[19]

A linear combination of the B_{1g} and B_{3u} modes describes the distortions observed in $Se_2(SCN)_6^{2-}$ and $Se_2(SeCN)_6^{2-}$.[5,20,21]

We are beginning a variable-temperature ^{125}Te and ^{13}C NMR study of these ions in solution in the hopes of elucidating the true mechanism(s) of dissociation.

Registry No. Tris(ethylenethiourea)tellurium(II) perchlorate, 72672-41-4; tris(trimethylenethiourea)tellurium(II) perchlorate, 72672-43-6.

Supplementary Material Available: Listings of observed and calculated structure factors and of calculated hydrogen atom positions (64 pages). Ordering information is given on any current masthead page.

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(17) Klaeboe, P.; Vikane, O. *Acta Chem. Scand., Ser. A* **1977**, *31*, 120 and references therein.

(18) Marøy, K., private communication, 1978.

(19) Herland, P.; Lundeland, M.; Marøy, K. *Acta Chem. Scand., Ser. A* **1976**, *30*, 719.

(20) Hauge, S.; Henriksen, P. A. *Acta Chem. Scand., Ser. A* **1975**, *29*, 778 and references therein.

(21) Hauge, S. *Acta Chem. Scand., Ser. A* **1975**, *29*, 843.

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Syntheses of $Mo(NC_6H_5)X_2(S_2CN(C_2H_5)_2)_2$ (X = Cl, Br) and the Structure of $Mo(NC_6H_5)Cl_2(S_2CN(C_2H_5)_2)_2 \cdot CHCl_3$

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Stable nitrene complexes of the type $Mo(NC_6H_5)X_2(S_2CN(C_2H_5)_2)_2$ (X = Cl, Br) have been prepared via several different synthetic routes. The structure of $Mo(NC_6H_5)Cl_2(S_2CN(C_2H_5)_2)_2 \cdot CHCl_3$ has been determined at −150 °C by X-ray diffraction techniques. The complex crystallizes in the monoclinic space group $P2_1/c$ with lattice constants of $a = 9.356$ (4) Å, $b = 16.088$ (7) Å, $c = 19.008$ (7) Å, and $\beta = 106.48$ (1)°. The structure was solved by using 4162 unique reflections having $F_o^2 > 3\sigma(F_o)^2$ and refined by using full-matrix, least-squares techniques to yield final discrepancy indices of $R(F) = 0.040$ and $R_w(F) = 0.055$. The coordination geometry around the molybdenum atom is close to pentagonal bipyramidal with the NC_6H_5 ligand and a chlorine atom occupying the apical sites. The short Mo–N distance of 1.734 (4) Å and the near-linearity of the Mo–N–C linkage (166.8 (3)°) suggest that the molybdenum–nitrogen bond has triple-bond character. The axial and equatorial Mo–Cl distances are identical, indicating that the linear $-NC_6H_5$ group exerts no significant trans influence. This result contrasts with the unequal Mo–Cl bond lengths (0.09 Å difference) in the oxo analogue $MoOCl_2(S_2CN(C_2H_5)_2)_2$.

Introduction

We have prepared a series of arylnitrene[1] complexes of molybdenum including $Mo(NAr)_2(Et_2dtc)_2$, $MoO(NAr)(Et_2dtc)_2$, $Mo(NAr)(Et_2dtc)_3^+$, $Mo(NAr)(Et_2dtp)_3$, and $Mo(NAr)Cl(Et_2dtp)_2$ in order to study the chemistry of the NR ligand and compare it to the oxo ligand in similar coordination environments.[2-4] The amphoteric nature of the

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(1) (a) Although IUPAC rules suggest that the name "imido" be used, we use herein the more familiar "nitrene" terminology which has found widespread acceptance; see a recent review by: Cenini, S.; La Monica, G. *Inorg. Chim. Acta* **1976**, *18*, 279. (b) Abbreviations used herein: Ar = aryl; Ph = C_6H_5; Et = C_2H_5; R = alkyl; X = Cl or Br; $R_2dtc = S_2CNR_2$; $R_2dtp = S_2P(OR)_2$; Cp = η^5-C_5H_5.

(2) Haymore, B. L.; Maatta, E. A.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1979**, *101*, 2063.

(3) Maatta, E. A.; Wentworth, R. A. D. *Inorg. Chem.* **1979**, *18* 2409.

(4) (a) Edelblut, A. W.; Wentworth, R. A. D., submitted for publication. (b) Maatta, E. A.; Haymore, B. L.; Wentworth, R. A. D. "Abstracts of Papers", 176th National Meeting of the American Chemical Society, Miami Beach, Fla., Sept 1978; American Chemical Society: Washington, D.C., 1978; INOR 38.