Contribution from the Department of Chemistry
University of South Carolina, Columbia, South Carolina 29208, U.S.A.

The Crystal and Molecular Structure of Tetrakis(Thiourea)Platinum(II) Chloride

R.L. Girling, K.K. Chatterjee, and E.L. Amma

Received December 15, 1972

The crystal structure of tetrakis(thiourea)platinum(II) chloride has been determined from 1991 counter measured intensities collected at room temperature. The structure was solved by heavy atom methods and refined by full matrix least-squares including anisotropic temperature factors and anomalous dispersion corrections for Pt, Cl and S to a final R of 0.054. The structure may be described in terms of $Pt[SC(NH_2)_2]_4^{2+}$ *ions and* Cl^- *anions with van der Waals interactions and N-H - - - Cl hdrogen bonding between ions. The shortest Pt-Cl distance is 3.773(7) Å. The* PtS_4 *is almost square planar with an 0.1 A displacement of S atoms from the least-squares plane. The entire cation has approximately* D_2 *symmetry. The average Pt-S distance is 2.313 A (all within 2 esd's, ± 0.006 A). One halogen seems to be involved in five hydrogen bonds (N-H - - - Cl, 3.5 A or less) and the other in three hydrogen bonds. The hydrogen bonding scheme seems to be the reason for the structural differences from the analogous Pd compounds.*

Introduction

Rather extensive structural studies of thiourea (tu) complexes$^{1-19}$ have been carried out in our laboratory and elsewhere. Experimental results have les us to speculate that the orientation of the thiourea group may be partly explained in terms of electronic effects. Simple Hückel calculations^{20} indicate "back-bonding" to ligand orbitals may be more costly in energy than back-bonding to sulfur d orbitals, thus explaining why the tu twists and/or tilts (defined below) to avoid overlap of the metal d and ligand π^* orbitals. Structural studies of the Mn^{II},^{3,8} Fe^{II},^{3,8} Co^{II},^{12} Cd^{II},^{3,8} Ni^{II},^{2} and Pd$^{II\,1}$ complexes show twisting and tilting to be independent of these metals. Examination of $Pt(tu)_4Cl_2$ was a logical extension of the nickel and palladium. Further examination, particularly in sixth period transition metals, seemed desirable especially to see if the softer metals had any noticeable effect on the tu orientation. In addition, this structure is not isomorphous with the previously reported analogous Pd compound.^{1,14}

Experimental Section

Tetrakis(thiourea)platinum(II) chloride, $Pt[SC(NH_2)_2]_4Cl_2$, was prepared by previously reported methods^{21} and single crystals were grown by crystallization from aqueous solution. The air-stable, yellow needle crystals were well formed rods of satisfactory quality for diffractometer data collection. Preliminary Weissenberg and precession data showed the crystals to be monoclinic with the systematic extinctions: for h0l, h = 2n+1, for 0k0, k = 2n+1, indicating the unique space group^{22} $P2_1/a$.

From calibrated precession photographs using Mo-Kα radiation (λ = 0.71068 A) at room temperature, the cell constants were found to be: a = 18.08 A, b = 10.17 A, c = 9.05 A, all ±0.02 A; β = 91.33°± 0.05°. The density measured by flotation, 2.24(3) g/cc, in a carbon tetrachloride-bromoform mixture is

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in good agreement with the calculated values of 2.27 g/cc based on four $Pt(tu)_4Cl_2$ entities per unit cell.

A single crystal 0.30×0.16×1.20 mm mounted about the long axis (c) was aligned on a Picker automated diffractometer by variations of well known methods.[23a] The intensities of 5000 independent reflections were recorded by the θ-2θ scan technique using Zr filtered MoKα radiation at room temperature. The peaks were scanned for 100 seconds (3.33° in 2θ) and backgrounds were estimated by stationary counting for 40 seconds at ±1.67° in 2θ of the peak maximum. Integrated intensities were calculated assuming a linear variation in background from the function: $I_{net} = I_{scan} - 1.25(B_1+B_2)$ where B_1 and B_2 are the backgrounds. Reflections were considered absent if I_{net} were less than $2\times1.25(B_1+B_2)^{1/2}$. Twelve equivalent reflections were measured and found to be within three times the error inherent in the counter statistics; otherwise, only one set of independent reflections to 2θ = 71° was measured. A standard reflection was measured every ten reflections to ensure stability of operation. Due to electronic difficulties with the scintillation crystal there were substantial differences in the standard peak during the entire period of the data collection. However, peak to peak variations were from 0.5 to 4 standard deviation (σ). The data were scaled to the standard peak measured during that particular data collection interval to ensure that any deviations caused by scintillation crystal difficulties were minimized.

The take-off angle, source-to-crystal, and crystal-to-counter values were 3.7°, 18cm, and 23 cm, respectively; and the receiving aperture at the counter was 6 mm wide by 8 mm high. The peak width at half peak height for an average reflection was 0.36° at the 3.7° take-off angle, indicating a reasonable mosaic width for the peaks. The counting rate never exceeded 5,000 count per second during the data collection, and no attenuators were used.

The linear absorption coefficient (μ) for this compound with MoKα radiation was calculated to be 97.7 cm^{-1}. No corrections were made for absorption.[23b] Anomalous dispersion effects were included in the refinement. Lorentz polarization correction were made.

Structure Solution

The structure was solved by conventional heavy atom techniques.[24a] Isotropic refinement[24b] of all atoms resulted in R = 0.094 and wR[24c] = 0.110. Converting to anisotropic temperature factors, a full matrix least-squares refinement reduced R to 0.054, wR to 0.071. A final difference map revealed no peak height corresponding to greater than 1.5 electrons.

The function minimized in the least-squares refinement was $\Sigma w(|F_O| - |F_C|)^2$ where F_O and F_C were the observed and calculated structure factors. Scattering factors for Pt^{2+}, Cl^-, and neutral sulfur, carbon and nitrogen were from Cromer and Waber.[25] The effects of anomalous dispersion were included in the structure factor calculations by addition to F_C;[26] the values for $\Delta f'$ and $\Delta f''$ for platinum, chlorine and sulfur were those given by Cromer.[27] The final tabulation of observed and calculated structure factors is listed in Table I. Unobserved data were not used in the structure refinement, but are included in the latter part of the F_O,F_C table. Final atomic positional and thermal parameters are listed in Table II. Interatomic distances and angles, dihedral angles between normals to planes, and their errors were computed[28] with the parameters and variance-covariance matrix from the last cycle of least-squares refinement and are listed in Tables III and IVb. RMS displacements are listed in Table IV.

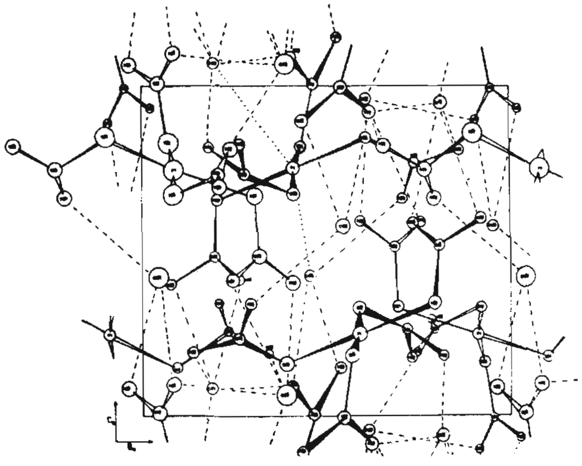

Figure 1. A perspective view of the contents of the unit cell down the [100] direction. Dashed lines indicate possible N-H-Cl hydrogen bonds. (For distances see Table III). Each Cl(1) seems to form five hydrogen bonds: N(6)-H--Cl(1), N(1)-H--Cl(1), N(8)-H--Cl(1), N(3)-H--Cl(1), and N(4)-H---Cl(1). Each Cl(2) seems to be involved in three hydrogen bonds: N(1)-H--Cl(2), N(2)-H--Cl(2) and N(7)-H--Cl(2). N(5) is the only nitrogen not appearing to be involved in hydrogen bonds. The dotted line indicates the shortest Cl-Pt distances for one of the Pt atoms.

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(23) (a) T.C. Furnas, Jr., « Single Crystal Orienter Instruction Manual », General Electric Co., Milwaukee, Wis., 1957.

(b) The neglect of absorption corrections probably makes our estimate of error optimistic and imposes some uncertainty in our reported rms displacements. However, our prime interest in this compound is in the arrangement of ligands about Pt+2 and the hydrogen bonding arrangement. In the light of the difficulties during data collection, we did not feel that further correction and refinement was desired nor warranted.

(24) (a) Patterson and electron density calculation done on an IBM 7040 with ERFR-3 program. A modification of the ERFR-2 of Sly, Shoemaker and van den Hende by D.R. Harrisi.

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c) $R = (\Sigma||F_O|-|F_C||)/\Sigma|F_O|$. Weighted $R = \{[\Sigma w(F_O-F_C)^2]/\Sigma wF_O^2\}^{1/2}$. Standard Error $= \frac{[\Sigma w(F_O-F_C)^2]^{1/2}}{C \times SF}$ / (NO-NV) where NO = number of observations; NV = number of variables; SF = scale factor; C = 1 if non-centric, 2 if centric; $w = 1/\sigma^2(F)$ $\sigma(F) = 1/F(Lp)\,[I(scan) + T_1/T_2\,(B) + D_{ig}^2\,I(scan)^2]^{1/2}$ where T_1 and T_2 are the total scan and total background times, respectively; 1/Lp = Lorentz-polarization correction; B = background count; I(scan) = scan counts; D_{ig} = constant usually 0.03 to approximate instrumental error.

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Table Ia. Observed and Calculated Structure Factors for Pt(thiourea)$_4$Cl$_2$. First column is h followed by F(obs) and F(calc). F(calc) = 10F(calc)$_{\text{absolute}}$.

Table Ib. Unobserved Reflections with Calculated Value Greater than F_{min}. First column is h followed by k and F(calc) = 5F(calc)$_{absolute}$. F_{min} = 172. Number of reflections less than F_{min} ≈ 2046. Unobserved reflections were not included in the refinement.

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                       Fmin ≤ |F(calc)| < 2.0 x Fmin                         (66)

  L =  0   -9  4 250 -17  1-222   8  3 329  12  4 264  -4  0-227  -1  5-246
 2  0 303  -7  4-308  14  9-186  12  3-194  13  4-241  -2  0-333  -2  7 217
 4  6 317  -6  4 174   2 13 181  14  3-286  16  4-198  -4  7-193  -3  8 319
 8 13-219  -5  4-332   4 13 196  18  3 174  10  6 283   6  9-239  -1  8 175
  L =  1   -4  4-237    L =  5   20  3 225  12  6 273  10  9 200    L =  9
-10  0-175   L =  2   10  0 196   3  4-329  16  6-175  12  9 191  -4  0 211
 -4  3-296 17  1 311   4  2-242   4  4-322   4  7 283  -3 11-196    L = 10
-15  4-259   L =  3    6  2 175   5  4-189   5  7-300   3 11 223 -10  0-249
-14  4-261 -16  1 204   7  2-320   6  4-217  11  7 183  -2 12-172  -4  0 268
-11  4 242 -15  1-244  12  2-193   9  4 202  12 10-217    L =  8   -3  2 221
-10  4 210   L =  4     L =  6   10  4 247    L =  7   -4  0-223  -2  3 299


                 2.0 x Fmin ≤ |F(calc)| < 3.0 x Fmin                 (7)

  L =  1   -8  4 499   5  2-478   L =  6    6  6-351  -2  0 344
 -6  3-471   L =  5   11  2 456   4  3-445   L =  9


                    3.0 x Fmin ≤ |F(calc)|                           (10)

  L =  0    1  1 625   L =  2    -8  0 827   L =  5     2  3-560
 4  0-584   L =  1    -6  0 813  -2  0-790   3  1-648
 6  0-895   8  0 577   L =  3     2  0 868   L =  6
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Table II. Final Atomic Positional and Thermal Parameters and Estimated Standard Deviations (esd of last figure in parentheses) anisotropic temperature factors of the form: $\exp-[\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl]$.

Atom	x	y	z	Atom	x	y	z
Pt	0.4071(01)	0.4099(01)	0.7514(01)	S(3)	0.5272(03)	0.4110(06)	0.6719(07)
Cl(1)	0.4169(03)	0.1112(05)	1.0730(07)	C(3)	0.5767(11)	0.2746(18)	0.7334(26)
Cl(2)	0.2758(04)	0.4583(06)	0.4258(08)	N(5)	0.6455(10)	0.2670(21)	0.7052(27)
S(1)	0.2860(03)	0.4295(06)	0.8278(08)	N(6)	0.5451(14)	0.1820(18)	0.8160(27)
C(1)	0.2901(12)	0.4576(23)	1.0183(28)	S(4)	0.4389(03)	0.6130(05)	0.8507(08)
N(1)	0.3466(12)	0.4041(27)	1.1024(27)	C(4)	0.3839(16)	0.7347(21)	0.7612(34)
N(2)	0.2413(11)	0.5303(21)	1.0760(24)	N(7)	0.3322(13)	0.7124(22)	0.6640(32)
S(2)	0.3732(03)	0.2029(05)	0.6667(07)	N(8)	0.4082(16)	0.8597(18)	0.7996(29)
C(2)	0.3931(11)	0.1877(21)	0.4821(26)	N(4)	0.4381(10)	0.2581(20)	0.4101(23)
N(3)	0.3540(13)	0.0883(23)	0.4110(23)				

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.0011(01)	0.0028(01)	0.0054(01)	0.0002(01)	0.0003(01)	0.0001(01)
Cl(2)	0.0024(02)	0.0062(05)	0.0066(10)	0.0006(03)	0.0003(04)	0.0004(05)
S(1)	0.0013(02)	0.0069(06)	0.0065(10)	0.0004(02)	0.0004(03)	0.0014(06)
S(2)	0.0028(02)	0.0044(05)	0.0030(09)	0.0011(02)	0.0000(03)	0.0002(05)
S(3)	0.0012(01)	0.0038(04)	0.0101(09)	0.0002(03)	0.0000(03)	0.0018(06)
S(4)	0.0018(01)	0.0037(05)	0.0081(11)	0.0001(02)	0.0017(03)	0.0005(06)
Cl(1)	0.0018(01)	0.0040(05)	0.0064(09)	0.0001(02)	0.0004(03)	0.0000(04)
C(1)	0.0012(06)	0.0066(20)	0.0060(39)	0.0011(08)	0.0009(11)	0.0014(22)
N(1)	0.0033(08)	0.0098(25)	0.0078(39)	0.0023(14)	0.0025(14)	0.0002(28)
N(2)	0.0016(05)	0.0078(21)	0.0063(34)	0.0001(09)	0.0001(11)	0.0003(21)
C(2)	0.0014(05)	0.0051(20)	0.0031(36)	0.0008(08)	0.0004(11)	0.0004(19)
N(3)	0.0042(09)	0.0068(20)	0.0051(32)	0.0041(12)	0.0016(13)	0.0039(24)
N(4)	0.0017(05)	0.0072(20)	0.0067(34)	0.0014(09)	0.0002(11)	0.0011(20)
C(3)	0.0016(06)	0.0028(14)	0.0028(33)	0.0002(06)	0.0016(11)	0.0005(17)
N(5)	0.0015(06)	0.0060(20)	0.0158(48)	0.0014(08)	0.0001(13)	0.0019(23)
N(6)	0.0044(06)	0.0032(19)	0.0061(48)	0.0002(07)	0.0006(12)	0.0001(21)
C(4)	0.0035(10)	0.0021(17)	0.0139(55)	0.0015(10)	0.0013(20)	0.0020(23)
N(7)	0.0028(08)	0.0066(22)	0.0160(54)	0.0013(11)	0.0035(16)	0.0003(27)
N(8)	0.0056(12)	0.0020(15)	0.0138(48)	0.0003(11)	0.0001(20)	0.0010(20)

Structure Description

Essentially the structure of $Pt(tu)_4Cl_2$ consists of molecular ions of $Pt(tu)_4^{2+}$ and chloride anions (Figure 1). The anions, ocupying non-axial positions relative to the plane of the platinum and four sulfurs, show long metal-halogen distances indicating only van der Waals interactions[33] between platinum and chlor-

Table III. Interatomic Distances, Angles and esd's.

Bonded Distances	
Pt-S(1)	2.321(06)
S(1)-C(1)	1.747(26)
N(1)-C(1)	1.372(30)
N(2)-C(1)	1.272(26)
Pt-S(2)	2.318(05)
S(2)-C(2)	1.724(23)
C(2)-N(3)	1.383(27)
C(2)-N(4)	1.274(26)
S(3)-Pt	2.302(05)
S(3)-C(3)	1.736(19)
C(3)-N(5)	1.276(27)
C(3)-N(6)	1.338(26)
Pt-S(4)	2.320(05)
S(4)-C(4)	1.771(28)
N(7)-C(4)	1.289(35)
N(8)-C(4)	1.386(30)
Angles (degrees)	
S(1)-C(1)-N(1)	119.7(16)
S(1)-C(1)-N(2)	119.0(20)
N(1)-C(1)-N(2)	119.0(20)
S(2)-C(2)-N(3)	113.5(15)
S(2)-C(2)-N(4)	126.5(18)
N(3)-C(2)-N(4)	119.8(21)
S(3)-C(3)-N(5)	118.7(17)
S(3)-C(3)-N(6)	121.1(16)
N(5)-C(3)-N(6)	119.9(20)
S(4)C-(4)-N(7)	125.4(18)
S(4)-C(4)-N(8)	110.7(22)
N(7)-C(4)-N(8)	123.5(25)
Cl(1)-Pt-Cl(2)	130.5(01)
Cl(1)-Pt-S(2)	65.1(01)
Cl(1)-Pt-S(1)	83.1(01)
Cl(1)-Pt-S(3)	101.2(17)
Cl(1)-Pt-S(4)	111.6(19)
Cl(2)-Pt-S(2)	72.7(01)
Cl(2)-Pt-S(1)	68.9(02)
Cl(2)-Pt-S(3)	109.6(01)
Pt-S(4)-C(4)	108.2(09)
Pt-S(1)-C(1)	106.8(07)
Pt-S(2)-C(2)	110.0(07)
Pt-S(3)-C(3)	112.2(07)
S(1)-Pt-S(2)	86.1(02)
S(1)-Pt-S(3)	174.7(02)
S(1)-Pt-S(4)	92.0(02)
S(2)-Pt-S(3)	98.3(02)
S(2)-Pt-S(4)	176.4(02)
S(3)-Pt-S(4)	83.6(02)
Intramolecular Non-Bonded Distance	
Pt-Cl(1)	4.207(05)
S(1)-Cl(2)	3.650(10)
Pt-C(1)	3.284(20)
Pt-N(1)	3.384(24)
S(1)-N(1)	2.705(24)
N(2)-S(1)	2.613(21)
N(2)-N(1)	2.303(29)
S(2)-Cl(1)	3.858(09)
S(2)-Cl(2)	3.796(09)
S(2)-S(1)	3.167(08)
Pt-C(2)	3.328(22)
Cl(2)-C(2)	3.503(23)
S(2)-N(3)	2.606(20)
Pt-N(4)	3.509(20)
N(4)-S(2)	2.685(21)
N(4)-N(3)	2.300(26)
S(3)-S(2)	3.497(08)
S(3)-N(4)	3.232(20)
C(3)-Pt	3.368(19)
C(3)-S(2)	3.786(19)
C(3)-N(4)	3.812(29)
S(3)-C(2)	3.713(23)
Pt-Cl(2)	3.773(07)
S(3)-N(5)	2.603(19)
Pt-N(6)	3.445(22)
Cl(1)-N(6)	3.399(19)
S(2)-N(6)	3.367(24)
S(3)-N(6)	2.685(17)
N(6)-N(5)	2.264(29)
S(4)-S(1)	3.338(07)
S(4)-C(1)	3.498(23)
S(4)-N(1)	3.559(27)
S(4)-S(3)	3.083(08)
Pt-C(4)	3.331(22)
C(4)-S(1)	3.630(22)
Pt-N(7)	3.446(21)
N(7)-Cl(2)	3.501(26)
N(7)-S(1)	3.351(26)
N(7)-S(4)	2.729(23)
S(4)-N(8)	2.608(20)
N(7)-N(8)	2.358(36)
Possible Intermolecular Hydrogen Bonded Distances*	
N(1)-Cl(1)	3.242(25)
N(6)-Cl(1)	3.399(19)
N(8)-Cl(1')	3.560(23)
N(4)-Cl(1'')	3.410(21)
N(3)-Cl(1'')	3.296(20)
N(7)-Cl(2)	3.502(26)
N(1'')-Cl(2)	3.269(25)
N(2'')-Cl(2)	3.295(23)

* Single prime is related to tabulated coordinates by transformation x,y,z; Double prime is related to tabulated coordinates by x, y, z-1.

Table IV. RMS Component of Thermal Displacement Along Principal Axes (A) (esd in parentheses).

Atom	1	2	3	Atom	1	2	3
Pt	0.115(01)	0.136(01)	0.155(01)	C(4)	0.067(60)	0.233(37)	0.262(45)
Cl(1)	0.144(09)	0.155(13)	0.184(07)	N(1)	0.124(56)	0.205(36)	0.286(34)
Cl(2)	0.162(14)	0.172(08)	0.212(08)	N(2)	0.161(37)	0.165(32)	0.202(27)
S(1)	0.131(11)	0.168(08)	0.200(09)	N(3)	0.070(70)	0.147(35)	0.315(32)
S(2)	0.112(17)	0.139(08)	0.224(08)	N(4)	0.129(36)	0.173(33)	0.218(28)
S(3)	0.126(10)	0.150(08)	0.212(10)	N(5)	0.117(35)	0.201(29)	0.261(39)
S(4)	0.125(11)	0.146(09)	0.219(07)	N(6)	0.128(38)	0.158(30)	0.272(35)
C(1)	0.092(45)	0.173(50)	0.202(29)	N(7)	0.135(40)	0.204(34)	0.300(34)
C(2)	0.104(51)	0.141(39)	0.182(30)	N(8)	0.100(40)	0.240(42)	0.306(32)
C(3)	0.055(129)	0.120(31)	0.190(32)				

ine. The platinum and four sulfur atoms in the cation show essentially square planar coordination (Figure 2). However, the sulfur-platinum-sulfur angles are significantly distorted from the ideal value of 90°, and there is also a slight tetrahedral distortion about the platinum, with the sulfur atoms displaced about 0.1 A from coplanarity. The $Pttu_4^{2+}$ cation approaches approximate D_2 molecular symmetry. The thiourea groups are planar within two standard deviations [29] and are roughly related to each other by the pseudorotation axes. Two of the groups are twisted and tilted up and the other two down. The dihedral angles between the planes of tu groups 1,2,3 and 4 (tu groups are assigned the same number as the sulfur atom in that group) and the plane calculated from the platinum and four sulfur atoms are 71.1°, 48.6°, 54.5° and 61.5°, respectively. These angles show the combined twist and tilt values of the tu group relative to the plane through the platinum and four sulfurs. Tilt values (rotation around the platinum-sulfur axis) can be estimated by the dihedral angle between the Pt-S(1)-S(2)-S(3)-S(4) plane and each platinum-sulfur-carbon plane (Figure 3). One method of finding the twist (rotation around the sulfur-carbon bond) is from the dihedral angles between the appropriate platinum-sulfur-carbon and tu planes (Figure 3). The four independent platinum-sulfur distances do not differ significantly from each other,

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(29) W.A. Spofford, « A Fortran Least-Square Plane Program for the IBM 1620», unpublished results (1968).

but their average value of 2.313 A is somewhat shorter than the sum of the covalent radii[30] which is 2.36 A. Intramolecular sulfur-sulfur distances are rather short, ranging from 0.62 to 0.20 A shorter than the sum of the van der Waals radii (3.70 A).[30] The differences among the platinum-sulfur-carbon angles are significant, the highest being 112.2(7)°, the lowest 106.8(7)°. In the tu groups the average values of the sulfur-carbon and carbon-nitrogen distances correspond within one standard deviation to the distances found in free thiourea by Truter.[31] The angles in two of the tu groups show no real distortion from 120°. However in groups 2 and 4 there is significant distortion from 120° in both the sulfur-carbon-nitrogen angles. Both show the same sort of distortion; the sulfur-carbon-nitrogen angle nearest the platinum being opened up about 5° and the other closed down approximately 9°. A number of short intramolecular and intermolecular chlorine-nitrogen and sulfur-nitrogen distances which indicate probable hydrogen bonding can be found in Table III.

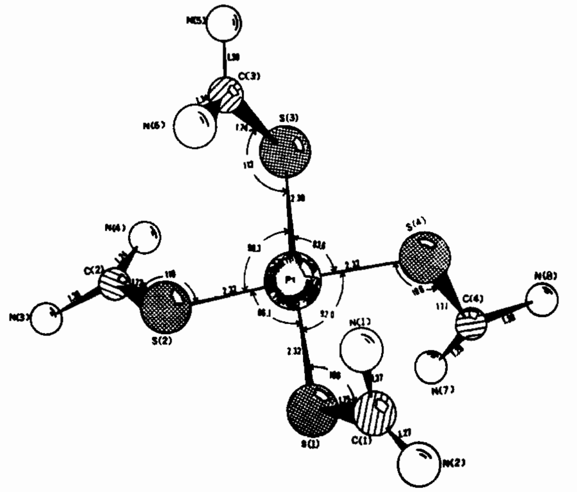

Figure 2. A perspective view of the $Pt[SC(NH_2)_2]_4$ cation showing relevant distances and angles. The molecular ion has approximate D_2 symmetry.

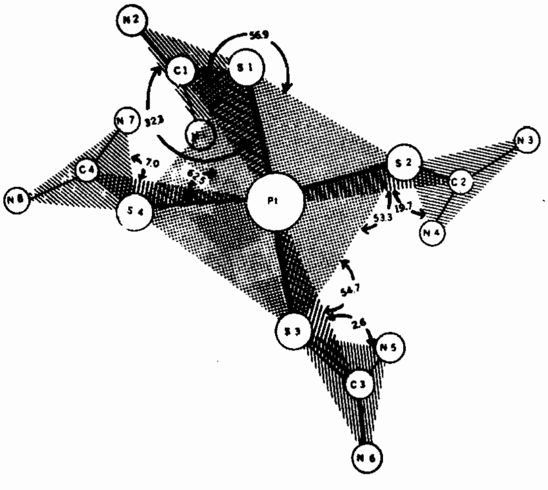

Figure 3 .Dihedral angles between relevant planes. Shown are the «twist» and «tilt» angles as defined in the text which completely specify the orientation of the tu ligand.

Discussion

Bonding in the $Pt(tu)_4^{2+}$ unit appears to be what we have come to expect in transition metal tu complexes.[1-4,12,17,32-34] The platinum-sulfur distances are slightly shorter than the sum of the normal single bond covalent radii.[30] The metal-sulfur-carbon angles are somewhat less than one would predict on the basis of simple sp^2 hybridization of the sulfur atom. Idealized sp^2 hybridization would also call for a twist dihedral angle of zero, the angle averages 15°. Hence, some other interaction must be affecting the tu groups.

In general, complexes of Pt^{2+} and Pd^{2+} with the same ligands are structurally so similar that they are crystallographically isomorphous. In the case of the present structure $Pttu_4Cl_2$ and $Pdtu_4Cl_2$[1] this is not the case. There are actually two striking differences between these structures: 1) The Pd^{2+} site defines an approximate center of symmetry for the complex as a whole whereas the Pt^{2+} site defines a site of approximate $D_2(222)$ symmetry; 2) The Cl-Pd-Cl angle is 179.2(1)° and is approximately perpendicular to the PdS_4 plane while the Cl-Pt-Cl angle is 130.5(1)° and the Cl-Pt bond is nowhere near perpendicular to the PtS_4 plane. A minor difference is that in $Pdtu_4Cl_2$ each halogen is involved with four hydrogen bonds and in the present structure Cl(1) seems to be involved in five and Cl(2) in three hydrogen bonds. Three forces which could affect the orientation of the four tu groups are: molecular packing forces, hydrogen bonding and electronic effects in the M-S bonds. Although it is clear that the crystal structures of $Pttu_4Cl_2$ and $Pdtu_4Cl_2$ are different, how the interplay of these forces bring this about is not obvious at this time. Subtle differences in hydrogen bonding and packing have been used to account for the fact that $Cotu_2Cl_2$[32] and $Zntu_2Cl_2$[33] are not isomorphous, whereas $Co(s\text{-}DEtu)_2Cl_2$ and $Zn(s\text{-}DEtu)_2Cl_2$[34] are isomorphous (s-DEtu = NN'-diethylthiourea).

Acknowledgment. We are grateful to the National Institutes of Health Grant No. GM-13985.

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(30) L. Pauling, «The Nature of the Chemical Bond», 3rd ed., Cornell University Press, Ithaca, N.Y., 1960 Chapt. 7, p. 260.
(31) M.R. Truter, *Acta Cryst.*, *22*, 556 (1967).
(32 D. De W. Hall and W. DeW. Horrocks, Jr., *Inoirg. Chem.*, *8*, 1809 (1969).
(33)R. Kuncher and M.R. Truter, *J. Chem. Soc.*, 3478 (1958).
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