Table VII. Possible A-H···B Hydrogen Bonds[a]

A	H	B	A···B, Å	Angle around H, deg
N(1)	H(1)	O(2)	3.12[b]	160
N(1)	H(2)	O(8)	3.07[c]	123
N(2)	H(3)	O(4)	3.06[b]	159
N(2)	H(4)	O(5)	3.07[b]	121
N(3)	H(5)	O(3)	3.10[b]	140
N(3)	H(6)	O(1)	3.16[b]	165
N(4)	H(7)	O(7)	3.13[c]	132
N(4)	H(8)	O(4)	3.02[b]	155

[a] Only interactions with A···B $\leq$ 3.2 Å and A-H···B > 120° are listed. [b] Interionic interaction. [c] Intraionic interaction.

four O atoms are involved in hydrogen bonding. For D there are only three strong hydrogen bonds and one of the O atoms is not involved in the network. The coordinated ClO_4^- ion of C is also involved in hydrogen bonding. Atoms O(7) and O(8) form intraionic hydrogen bonds and O(5) is involved in an interionic hydrogen bond. This extensive network of hydrogen bonds produces that rare crystallographic treat—ordered perchlorate ions. Figure 3 shows a portion of the interionic hydrogen-bonding scheme. The distances and angles in the perchlorate ions are summarized in Tables II and III.

In summary, this work has shown that C adopts six-coordinate geometry in the solid state by stabilizing the weakly bound ClO_4^- ligand via hydrogen bonding with the en ligands coordinated to cobalt. Thus, there is still no well documented example of a ligand system that produces both five- and six-coordinate {CoNO}^{8} complexes with tetragonal geomtry about a strongly bent CoNO group. However, it may still be possible to isolate the five-coordinate $[Co(NO)(en)_2]^{2+}$ cation by using large counterions which cannot form hydrogen bonds and do not usually serve as ligands in metal complexes.

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Registry No. Co(NO)(en)$_2$(ClO$_4$)$_2$, 60384-76-1.

Supplementary Material Available: Listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Presented in part at the 1974 spring meeting of the American Crystallographic Association: J. H. Enemark and R. D. Feltham, Abstracts, Spring 1974 Meeting, American Crystallographic Association, Vol. 2, p 107.

(2) The superscript 8 in {CoNO}^{8} refers to the total number of electrons that are primarily associated with metal d and π^*(NO) orbitals. For a more thorough discussion see ref 3 and 4.

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Structure of Bis(2-thiouracil)chlorocopper(I) Dimethylformamide Solvate, a Reaction Product of Copper(II) Chloride with Thiouracil

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The structure of bis(2-thiouracil)chlorocopper(I) dimethylformamide solvate has been solved and refined by full-matrix least squares to a final convention residual of 0.055. The structure consists of almost planar molecular units of bis(2-thiouracil)chlorocopper(I) with the molecules of solvation occupying a cavity. Base stacking and hydrogen bonding also contribute to the stability of the crystal structure. The Cu(I) moiety is three-coordinate planar with two sulfurs and one chlorine coordinated to the metal. The Cu-S and Cu-Cl distances are 2.228 (1), 2.225 (1), and 2.260 (1) Å, respectively. Crystal data are as follows: a = 12.165 (3) Å, b = 11.362 (4) Å, c = 14.565 (4) Å, β = 122.99 (2)°, Z = 4, space group $P2_1/c$, d_{measd} = 1.68 g cm^{-3}, d_{calcd} = 1.64 g cm^{-3}; number of observed reflections 2902.

Introduction

The interaction between the minor base of the nucleic acids 2-thiouracil and Cu^{2+} and Cu^+ is of considerable biological interest for several reasons. Thiouracils are minor components of tRNA in both *Escherichia coli* and mammalian tissue[1-3] and the interaction of metal ions with tRNA is of importance in protein synthesis and consequently cell growth.[4,5] In addition, derivatives of 2-thiouracils are the drugs of choice in the treatment of hyperthyroid conditions[6] and elevated copper levels are observed in conjunction with these conditions.[7,8] Copper has been implicated in thyroid function at the level of iodine production,[9] the same level at which the thiouracil is thought to function. Hence, removal of cupric or cuprous ion by complexation could be an alternate possible mode of

Table I. I[a–c]

Final Atomic Positional Parameters and Estimated Standard Deviations

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu	0.021 96 (7)	0.093 48 (5)	0.123 63 (7)	H(14)	0.533 (5)	−0.247 (4)	0.274 (4)
Cl	0.202 4 (1)	0.204 6 (1)	0.181 7 (1)	H(15)	0.351 (6)	−0.382 (6)	0.194 (5)
S(1)	0.035 1 (1)	−0.102 2 (1)	0.130 9 (1)	H(16)	0.154 (4)	−0.306 (3)	0.154 (3)
S(2)	−0.164 3 (1)	0.176 4 (1)	0.085 0 (1)	H(22)	0.027 (5)	0.347 (6)	0.120 (5)
C(11)	0.189 8 (4)	−0.141 3 (4)	0.177 0 (4)	H(24)	−0.142 (5)	0.659 (6)	0.076 (5)
N(12)	0.289 8 (4)	−0.065 1 (4)	0.211 3 (4)	H(25)	−0.322 (6)	0.549 (5)	0.029 (5)
C(13)	0.420 0 (5)	−0.093 9 (5)	0.249 5 (5)	H(26)	−0.350 (5)	0.350 (5)	0.028 (4)
C(14)	0.440 0 (5)	−0.218 5 (5)	0.242 6 (5)	O(31)	−0.4835 (4)	0.3053 (3)	0.0194 (3)
C(15)	0.342 8 (5)	−0.294 4 (5)	0.209 6 (5)	C(32)	0.4782 (6)	0.2798 (5)	0.4583 (5)
N(16)	0.219 7 (4)	−0.257 0 (3)	0.179 0 (4)	N(33)	0.3889 (4)	0.3571 (4)	0.4422 (4)
O(17)	0.501 5 (4)	−0.017 5 (4)	0.281 0 (4)	C(34)	0.3448 (8)	0.4495 (6)	0.3617 (6)
C(21)	−0.151 7 (4)	0.325 6 (4)	0.083 4 (4)	C(35)	0.3220 (7)	0.3473 (7)	0.4973 (7)
N(22)	−0.041 7 (4)	0.379 4 (3)	0.104 8 (4)	H(32)	0.515 (–)	0.300 (–)	0.413 (–)
C(23)	−0.024 9 (5)	0.500 9 (4)	0.104 3 (4)	H(341)	0.252 (–)	0.435 (–)	0.300 (–)
C(24)	−0.137 8 (6)	0.567 6 (5)	0.076 9 (6)	H(342)	0.403 (–)	0.451 (–)	0.331 (–)
C(25)	−0.246 9 (5)	0.514 0 (5)	0.054 2 (6)	H(343)	0.351 (–)	0.528 (–)	0.396 (–)
C(26)	−0.253 4 (4)	0.393 5 (3)	0.058 0 (4)	H(351)	0.332 (–)	0.422 (–)	0.538 (–)
O(27)	−0.081 7 (3)	0.038 9 (3)	0.373 3 (3)	H(352)	0.357 (–)	0.280 (–)	0.550 (–)
H(12)	−0.279 (6)	0.003 (5)	0.208 (5)	H(353)	0.225 (–)	0.334 (–)	0.442 (–)

Thermal Parameters and Estimated Standard Deviations[d]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	72 (1)	36 (1)	124 (1)	4 (1)	48 (1)	1 (1)
Cl	68 (1)	40 (1)	119 (2)	−8 (1)	48 (1)	−12 (1)
S(1)	50 (1)	35 (1)	110 (2)	−2 (1)	39 (1)	4 (1)
S(2)	69 (1)	32 (1)	101 (1)	5 (1)	53 (1)	2 (1)
C(11)	55 (5)	32 (3)	59 (4)	0 (3)	32 (4)	3 (3)
N(12)	56 (4)	33 (3)	81 (4)	−4 (3)	35 (4)	0 (3)
C(13)	59 (5)	60 (4)	82 (5)	7 (4)	43 (4)	13 (4)
C(14)	62 (5)	66 (5)	76 (5)	16 (4)	41 (5)	15 (4)
C(15)	84 (6)	46 (4)	70 (5)	20 (4)	48 (5)	11 (4)
N(16)	71 (4)	27 (3)	73 (4)	0 (3)	41 (4)	6 (3)
O(17)	47 (4)	54 (4)	116 (5)	−20 (3)	43 (4)	6 (3)
C(21)	50 (4)	37 (3)	58 (4)	−6 (3)	30 (4)	−1 (3)
N(22)	53 (4)	28 (3)	72 (4)	1 (3)	33 (3)	2 (3)
C(23)	79 (5)	31 (3)	72 (5)	2 (4)	39 (4)	0 (3)
C(24)	83 (6)	30 (4)	121 (7)	4 (4)	48 (5)	3 (4)
C(25)	64 (5)	48 (4)	114 (6)	19 (4)	45 (5)	9 (4)
N(26)	59 (4)	40 (3)	76 (4)	4 (3)	39 (3)	−3 (3)
O(27)	41 (3)	21 (3)	66 (4)	10 (2)	26 (3)	0 (2)
O(31)	50 (4)	52 (3)	54 (4)	−17 (3)	30 (3)	−15 (3)
C(32)	89 (6)	77 (5)	78 (5)	−3 (5)	56 (5)	−16 (4)
N(33)	77 (5)	62 (4)	65 (4)	7 (3)	37 (4)	−2 (3)
C(34)	294 (14)	100 (6)	142 (7)	55 (8)	109 (9)	16 (6)
C(35)	179 (10)	157 (9)	270 (11)	63 (8)	164 (10)	61 (9)

[a] Esd of last figure in parentheses. [b] First digit of atom designation is group number; second digit is atom number. Hydrogen atoms have the number of the atom they are attached to. [c] Hydrogen atoms on DMF not allowed to vary. [d] Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)] \times 10^4$.

action of thiouracil. We have been exploring the chemistry of the interaction between metal ions and 2-thiouracil and wish to report the details of the structure of a product of the reaction between Cu^{2+} and thiouracil.[10a]

In terms of inorganic chemistry thiouracil is closely related to thiourea and the latter ligand has led to a number of interesting Cu^+ complexes of unusual stereochemistry including polynuclear species.[10b]

Experimental Section

Preparation. Crystals of bis(2-thiouracil)chlorocopper(I) dimethylformamide solvate were prepared as follows. Solid thiouracil (0.02 mol) [Nutritional Biochemicals Co.] was slowly added to 100 ml of warm (70 °C) aqueous $CuCl_2$ (0.15 mol) solution. An amorphous yellow solid which formed within 5 min was collected and washed with water and carbon disulfide to remove any free sulfur. This solid is insoluble in most common solvents but was recrystallized from dimethylformamide by slow evaporation to yield light yellow crystals.

X-Ray Data. The clear light yellow air-stable approximately octahedral crystals were mounted on glass fibers and preliminary Weissenberg and precession photographs showed the crystals to be monoclinic with $0k0$ absences of $k = 2n + 1$ and $h0l$ absences of $l = 2n + 1$, corresponding to space group $P2_1/c$. Such an octahedral crystal of dimensions 0.27 × 0.40 × 0.39 mm bounded by planes $(\bar{1}11)$, (100), and (121) was aligned on a Picker card-controlled diffractometer by variations of well-known techniques[11] and used for intensity data collection. The lattice constants were determined by a least-squares refinement of the angles ϕ, θ, ω, and χ of 23 general reflections which had been accurately centered. By use of Mo Kα radiation (λ 0.710 68 Å) the lattice constants of the monoclinic cell at room temperature were determined to be $a = 12.165$ (3) Å, $b = 11.362$ (4) Å, $c = 14.565$ (4) Å, $\beta = 122.99$ (2)°. The experimental density d_{measd} is 1.68 g cm^{-3}; with four molecules of $Cu(C_4N_2OSH_4)_2Cl{\cdot}C_3NOH_7$ per unit cell, d_{calcd} is 1.64 g cm^{-3}. The intensities of 5050 crystallographically independent reflections were measured by the θ–2θ scan technique to a 2θ maximum of 60° using unfiltered Mo Kα (λ 0.710 68 Å) radiation at room temperature.[12a] The peaks were scanned for 44.9 s (2°/min) and backgrounds were estimated by stationary counting for 20 s at ±0.75° in 2θ from the peak maxima. Integrated intensities were calculated assuming a linear variation in background from the function $I_{\text{net}} = I_{\text{scan}} - 1.125(B_1 + B_2)$ where B_1 and B_2 are the background counts. Reflections were considered absent if the integrated intensity was less than $2.0[1.125^2(B_1 + B_2)]^{1/2}$ (2.0σ of background). Based on this criterion 2902 reflections were retained

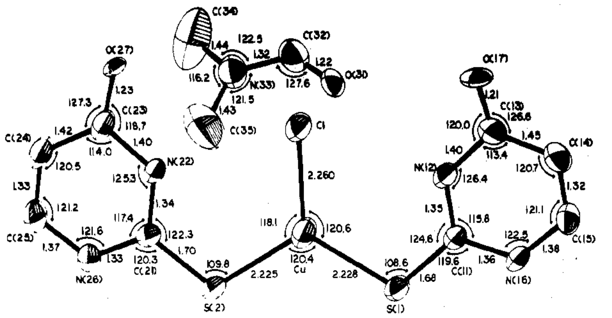

Figure 1. ORTEP[30] drawing of an isolated bis(2-thiouracil)-chlorocopper(I) molecule with its accompanying dimethylformamide molecule of solvation. Relevant distances and angles are shown. For esd's see Table III. The thermal ellipsoids are drawn at the 50% probability level.

and used in the structure solution and refinement. A standard reflection chosen of average intensity in the center of the χ, ϕ, and 2θ range was monitored after every tenth reflection and no decomposition or electronic malfunction was noted. The takeoff angle, source-to-crystal, and crystal-to-counter values were 3.7°, 18 cm, and 23 cm, respectively. The peak width at half-height for an average reflection was 0.32° in 2θ indicating a mosaic spread such that all reflections were counted during the scan. The counting rate did not exceed 5000 counts/s and no attenuators were used. The linear absorption coefficient (μ) for this compound with Mo Kα radiation was calculated to be 18.0 cm^{-1} and the transmission coefficient for the absorption correction[12b] using the above faces ranged from 0.940 to 0.962. The usual Lorentz–polarization corrections were made and the intensities were reduced to structure factors.

Structure Solution. The solution of the crystal structure of Cu(SUra)$_2$Cl·DMF was carried out by standard heavy-atom techniques in which the Cu, S, and Cl atoms were located from the three-dimensional Patterson function and the remaining atoms from three-dimensional electron density maps.[13] Refinement by full-matrix least squares[14] included anisotropic temperature factors for all nonhydrogen atoms and isotropic temperature factors for the hydrogen atoms on the thiouracil groups. Hydrogen atoms on the dimethylformamide were located from a difference Fourier, positionally idealized, assigned isotropic temperature factors of 5.9, and included in the final refinement. The refinement converged to final R and R_w of 0.055 and 0.062, respectively. A final difference Fourier was essentially featureless.

The function minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where w, F_o, and F_c are the weights based on counting statistics and the observed and calculated structure factors, respectively. Neutral atom scattering factors as given by Cromer and Waber[15] were used throughout. Corrections for the real and imaginary parts of the anomalous dispersion for Cu, Cl, and S, as given by Cromer,[16] were applied by addition to F_c. Final observed and calculated structure factors are listed elsewhere[17] along with the unobserved data which were not used in the refinement. Final atomic positional and thermal parameters are found in Table I. Interatomic distances, angles, dihedral angles between normals to planes, and their errors were computed using the parameters and variance–covariance matrix[18] from the last cycle of least squares and are found in Tables II and III.

Description and Discussion of Structure

The structure consists of nearly planar neutral bis(2-thiouracil)chlorocopper(I) molecules and molecules of di-

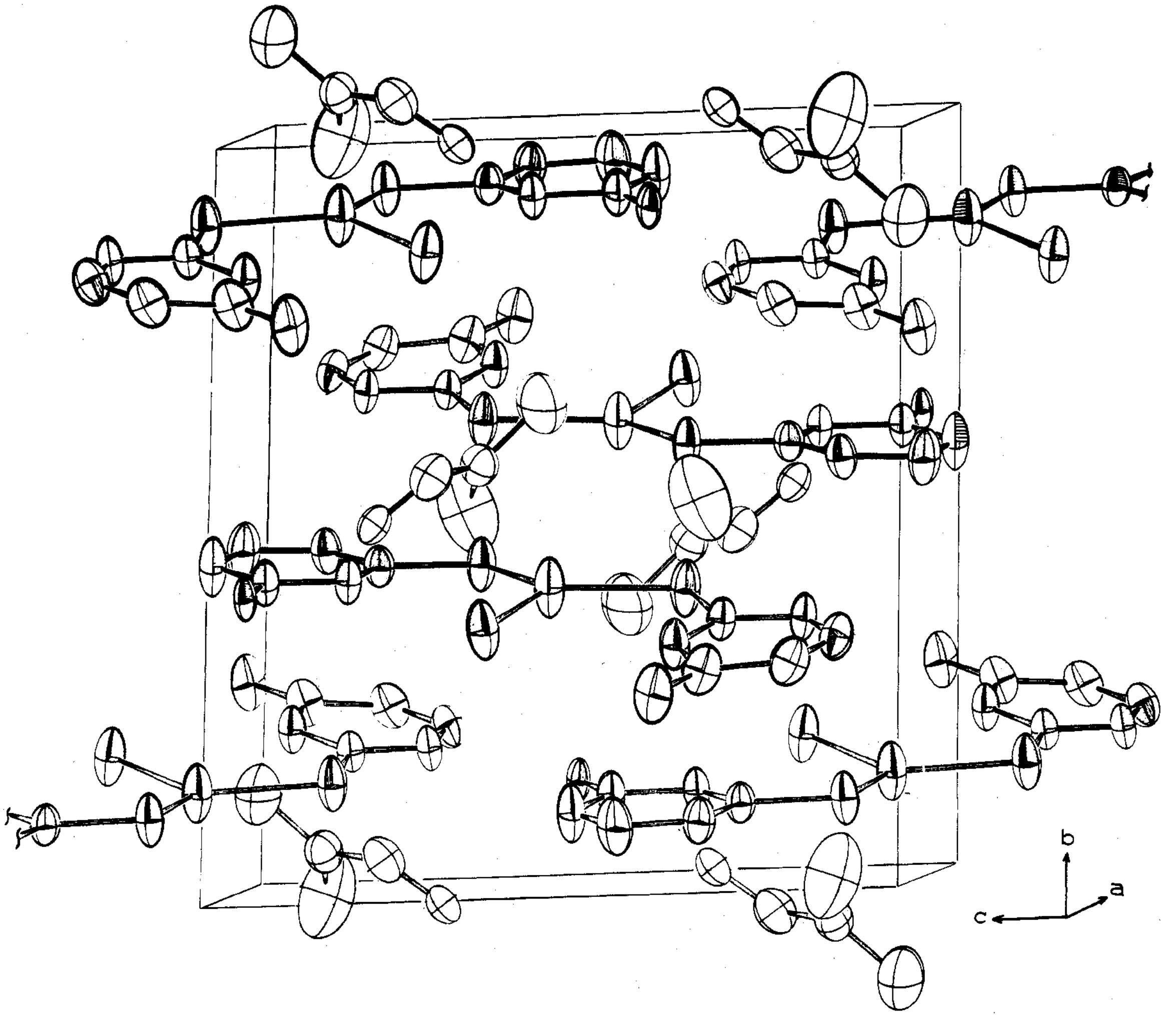

Figure 2. ORTEP drawing of the contents of the unit cell to indicate the packing of the planar molecules and the location of the molecules of solvation.

Table II. Interatomic Distances (Å) and Angles (deg) and Esd's[a,b]

Distances

Cu–Cl	2.260 (1)	C(25)–N(26)	1.374 (6)
Cu–S(1)	2.228 (1)	N(26)–C(21)	1.329 (6)
Cu–S(2)	2.225 (1)	C(23)–O(27)	1.231 (7)
S(1)–C(11)	1.677 (4)	O(31)–C(32)	1.221 (7)
C(11)–N(12)	1.349 (6)	C(32)–N(33)	1.315 (7)
N(12)–C(13)	1.402 (6)	N(33)–C(34)	1.441 (8)
C(13)–C(14)	1.449 (7)	N(33)–C(35)	1.425 (8)
C(14)–C(15)	1.324 (7)	N(12)–H(12)	0.78 (6)
C(15)–N(16)	1.377 (6)	C(14)–H(14)	1.01 (5)
N(16)–C(11)	1.359 (6)	C(15)–H(15)	1.04 (7)
C(13)–O(17)	1.205 (6)	N(16)–H(16)	0.88 (4)
S(2)–C(21)	1.704 (5)	N(22)–H(22)	0.82 (6)
C(21)–N(22)	1.344 (6)	C(24)–H(24)	1.03 (6)
N(22)–C(23)	1.397 (6)	C(25)–H(25)	0.88 (6)
C(23)–C(24)	1.421 (7)	N(26)–H(26)	1.12 (6)
C(24)–C(25)	1.329 (8)		

Angles

Cl–Cu–S(1)	120.64 (5)	C(25)–N(26)–C(21)	121.6 (4)
Cl–Cu–S(2)	118.14 (6)	O(31)–C(32)–N(33)	127.6 (5)
S(1)–Cu–S(2)	120.41 (5)	C(32)–N(33)–C(34)	122.5 (5)
Cu–S(1)–C(11)	108.6 (2)	C(32)–N(33)–C(35)	121.1 (5)
S(1)–C(11)–N(12)	124.6 (4)	C(34)–N(33)–C(35)	116.2 (5)
S(1)–C(11)–N(16)	119.6 (3)	C(11)–N(12)–H(12)	122 (4)
N(12)–C(11)–N(16)	115.8 (4)	C(13)–N(12)–H(12)	112 (4)
C(11)–N(12)–C(13)	126.4 (4)	C(13)–C(14)–H(14)	118 (3)
N(12)–C(13)–O(17)	120.0 (5)	C(15)–C(14)–H(14)	121 (3)
N(12)–C(13)–C(14)	113.4 (4)	C(14)–C(15)–H(15)	122 (3)
O(17)–C(13)–C(14)	126.6 (5)	N(16)–C(15)–H(15)	116 (4)
C(13)–C(14)–C(15)	120.7 (5)	C(15)–N(16)–H(16)	122 (3)
C(14)–C(15)–N(16)	121.1 (5)	C(11)–N(16)–H(16)	116 (3)
C(15)–N(16)–C(11)	122.5 (5)	C(21)–N(22)–H(22)	126 (5)
Cu–S(2)–C(21)	109.8 (2)	C(23)–N(22)–H(22)	108 (5)
S(2)–C(12)–N(22)	122.3 (3)	C(23)–C(24)–H(24)	125 (3)
S(2)–C(21)–N(26)	120.3 (3)	C(25)–C(24)–H(24)	115 (3)
N(22)–C(21)–N(26)	117.4 (4)	C(24)–C(25)–H(25)	125 (4)
C(21)–N(22)–C(23)	125.4 (4)	N(26)–C(25)–H(25)	114 (4)
N(22)–C(23)–O(27)	118.7 (5)	C(25)–N(26)–H(26)	119 (3)
N(22)–C(23)–C(24)	114.0 (5)	C(21)–N(26)–H(26)	118 (4)
O(27)–C(23)–C(24)	127.3 (5)	O(31)–C(32)–H(32)	111 (-)[c]
C(23)–C(24)–C(25)	120.5 (5)	N(33)–C(32)–H(32)	110 (-)[c]
C(24)–C(25)–N(26)	121.2 (5)		

Intermolecular Nonbonded Distances Less Than 3.4 Å

C(15)–O(27)	3.123 (8)	O(17)–C(23)	3.078 (9)
C(15)–O(17)	3.311 (9)	O(17)–O(17)	3.220 (9)
O(17)–N(16)	2.718 (8)	O(17)–N(22)	3.268 (8)

[a] Esd of last digit in parentheses. [b] Methyl hydrogen angles in DMF were set at 109° and not varied. [c] Hydrogen position was located on a difference Fourier map but not allowed to vary.

methylformamide as solvate. (Figure 1). These planar molecules are oriented such that there appears to be some base stacking between molecules (Figure 2) that contributes to the stabilization of the molelcular geometry as well as to the crystal stabilization (Table II). This base stacking probably contributes to the observation that the Cu and three S atoms and two pyrimidine rings are almost coplanar. In addition there seems to be a strong hydrogen bond contributing to the overall stabilization of the structure from O(17) to N(16) in the cell displaced one translation in the *b* direction at 2.72 (1) Å. The 2-thiouracil rings are in a cis configuration which leads to a pocket that contains the dimethylformamide molecule.

The local environment about the metal atom is three-coordinate planar with two sulfurs and a chlorine. This stereochemistry for Cu(I) was once thought unusual, but it has recently been found in a number of instances, particularly with soft ligands such as phosphorus or sulfur,[19-23] and is found even in polynuclear Cu(I) with such soft ligands.[24,25] The Cu–S and Cu–Cl distances are short—2.228 (1), 2.225 (1), and 2.260 (1) Å, respectively—compared to the sum of the single-bond covalent radii—2.39 and 2.41 Å. However, this shortening has been observed previously and can be attributed to the difference between three-coordinate planar[19-23] and four-coordinate "tetrahedral"[26,27] covalent radii of the metal. The geometry about the sulfur atom indicates that a sulfur sp^2 orbital and electron pair are involved in binding to copper. The C–S bonds at 1.677 (4) and 1.704 (5) Å are probably not distinguishable from the C–S distance in 2-thiouracil at 1.67 (1) Å.[28] They are both longer than the analogous bond in 2,4-dithiouracil [1.645 (6) Å[29]], but this C–S bond is not independent of the effects of the other C–S group in the molecule at 1.684 (6) Å and it would be incorrect to indicate that our C–S distance was elongated over free thiouracil. In general, metal–thiourea bonds with similar M–S–C geometries as in the present structure do not significantly affect S–C distances and the above result is not surprising.[26,27] The bond distances within the 2-thiouracil moieties indicate the molecules are clearly in the keto form. The 2-thiouracil moiety specified by atoms C(21)···N(22) is normal, but the remaining 2-thiouracil ring specified by atoms C(11)···N(12) is considerably distorted from planarity (Table III) probably due to a combination of hydrogen bonding involving N(16) and overcrowding between O(17) atoms on molecules in adjacent cells along *b*.

The stoichiometry and structure of this reaction product are typical of the reaction between Cu^{2+} and NC(=S)N systems, i.e., reduction of Cu^{2+} to Cu^{+} with concomitant oxidation of the C=S linkage to C–S–S–C^{+} dimers which are unreactive. The soft Cu^{+} then reacts with excess ligand to form an especially stable metal complex. It is clear that thiouracil is a capable scavenger of Cu^{2+} after reduction, or of Cu^{+} directly,

Table III. Least-Squares Planes of the Form $AX + BY + CZ = D$

Plane no.	Plane atoms	*A*	*B*	*C*	*D*	Displacement from plane (max), Å
I	C(11), N(12), C(13), C(14), C(15), N(16)	0.3341	0.0949	−0.9378	−1.8873	0.026 (9)
II	C(21), N(22), C(23), C(24), C(25), N(26)	0.2506	−0.0479	−0.9669	−1.7862	0.006 (9)
III	S(1), Cl, S(2)					
IV	S(1), Cl, C(11)					
V	S(2), Cl, C(21)					
VI	S(1), C(11), N(12)					
VII	S(2), C(21), N(22)					

Atoms out of planes	Dev, Å	Atoms out of planes	Dev, Å	Atoms out of planes	Dev, Å
Cu from III	0.116 (8)	S(1) from I	0.074 (8)	O(27) from II	−0.554 (9)
O(17) from I	1.013 (9)			S(2) from II	0.016 (9)

Planes	Dihedral angle, deg	Planes	Dihedral angle, deg	Planes	Dihedral angle, deg
III–IV	3 (1)	III–V	4 (1)	IV–VI	3 (1)
				V–VII	4 (1)

and could well perform these functions in the biological environment.

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Registry No. Cu(SUra)$_2$Cl·DMF, 60525-67-9.

Supplementary Material Available: Listing of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Diiodo(butane-1,4-diyl)bis(dimethylphenylphosphine)platinum(IV)[1]

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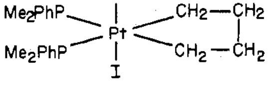
The Pt complex $C_{20}H_{30}P_2I_2Pt$ crystallizes in the monoclinic space group $C2/c$ with $a = 15.286$ Å, $b = 9.709$ Å, $c = 17.036$ Å, $\beta = 107.49°$, $d_{calcd} = 2.15$ g/cm^3 for $Z = 4$. X-ray diffraction intensity data were collected by an automated diffractometer using graphite-monochromated Mo Kα radiation. For 1575 reflections with $F^2 > 3\sigma(F^2)$, $R_1 = 0.035$ and $R_2 = 0.044$. The six-coordinate Pt atom is at the center of a distorted octahedron; the six neighbors of Pt are two phosphorus atoms at 2.418 (3) Å, two iodine atoms at 2.641 (1) Å, and two carbon atoms from the butanediyl ligand at 2.15 (1) Å. The complex has a crystallographic twofold axis that passes through the Pt atom.

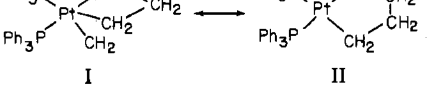
Introduction

In this paper we report the structure of a cyclic organoplatinum(IV) complex



Metallocyclic complexes of this general form have been postulated as intermediates in several transition metal complex catalyzed reactions. For example, they may be implicated in the isomerization of strained-ring carbocyclic compounds, in olefin metathesis, and in cycloaddition reactions of olefins. There is therefore a need for more information about the chemical properties and structures of these compounds.

It has previously been shown that the similar platinum(II) complex $[Pt(CH_2)_4(PPh_3)_2]$ has high thermal stability and decomposes to give mostly but-1-ene at 120 °C in dichloromethane.[2] The structure of the complex[3] is of particular interest in that it shows an unsymmetrical puckering of the $Pt(CH_2)_4$ ring. This puckering was considered to be the result of a contribution to the bonding from the canonical form I.



I II

The platinum(IV) complex $[PtI_2(CH_2)_4(PMe_2Ph)_2]$ has no vacant stereochemical position and is already an 18-electron complex. Thus a canonical form analogous to I can play no

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