Table I. Interatomic Distances[a] (Å) and Angles (deg) in the $(Fe_6S_6Cl_6)^{2-}$ (A) and $(Fe_6S_6Cl_6)^{3-}$ (B) Anions

	A[b]	B[c]
	Distances	
Fe–Fe[d]	3.791 (6,5)	3.790 (3,7)
Fe–Fe[e]	2.757 (6,5)	2.765 (3,3)
Fe–S[d]	2.268 (6,8)	2.284 (3,3)
Fe–S[e]	2.254 (12,8)	2.272 (6,2)
Fe–Cl	2.189 (6,8)	2.224 (3,2)
S–S[d]	3.743 (6,8)	3.801 (3,8)
S–S[e]	3.585 (6,8)	3.618 (3,5)
	Angles	
S–Fe–S[d]	112.0 (6,9)	113.7 (3,3)
S–Fe–S[e]	104.8 (12,5)	105.2 (6,2)
Fe–S–Fe[d]	114.5 (6,6)	113.2 (3,3)
Fe–S–Fe[e]	75.1 (12,4)	74.8 (6,2)
Fe–Fe–Fe[d]	60.0 (6,4)	60.0 (3,2)
Fe–Fe–Fe[e]	86.9 (6,5)	86.5 (3,3)

[a] See Figure 1 for the labeling scheme. The mean values of chemically equivalent bonds are given. In parenthesis the first entry represents the number of independent distances or angles averaged out, the second entry represents the larger of the standard deviations for an individual value estimated from the inverse matrix or of the standard deviation: $\sigma = [\sum^{N}{}_{i=1}(x_i - \bar{x})^2/N(N-1)]^{1/2}$. [b] This work. [c] From ref 8. [d] Distances or angles within the Fe_3S_3 structural units. [e] Distances or angles within the Fe_2S_2 rhombic units.

DMF) are unstable and the transformation of the $(Fe_6S_6X_6)^{2-}$ anions to the $(Fe_4S_4X_4)^{2-}$ clusters and unidentified byproducts is evident in electronic spectra changes. In the presence of excess X^- the transformation occurs quantitatively[13] according to eq 2.

$$(Fe_6S_6X_6)^{2-} + 2X^- \rightarrow (Fe_4S_4X_4)^{2-} + (Fe_2S_2X_4)^{2-} \quad (2)$$

The convenient, reliable synthesis of the $(Fe_6S_6X_6)^{2-}$ dianions allows for a new route for the synthesis of the corresponding trianions. The latter can be obtained in excellent yields by the $(R_4N)^+BH_4^-$ reduction of the dianions in CH_2Cl_2 solution ($R = C_2H_5$).

Single crystals of $(Ph_4P)_2(Fe_6S_6Cl_6)$ (III) were obtained by the slow diffusion of ether to a CH_2Cl_2 solution of this complex. In the crystal structure of III[14] the anion shows the same hexagonal prismatic Fe_6S_6 core reported for I[8] and II (Figure 1).[9] Selected structural parameters for the anion in III are compared to corresponding parameters in the anion of I (Table I).

Within the accuracy of the structure determinations, the Fe_6 distorted octahedra in I and III have indistinguishable Fe–Fe distances and Fe–Fe–Fe angles. The Fe–S, Fe–Cl, and S–S distances in I, however, are slightly longer than those in III, and collectively these differences may be statistically significant. The shorter Fe–S distances in III possibly reflect the higher formal charge (evident in the Mössbauer spectra isomer shift (IS) values) for the iron atoms in this cluster.

The Mössbauer spectra of III at 125 K (vs. Fe) display one quadrupole doublet with IS and ΔE_Q values of 0.425 (1) and 0.616 (1) mm/s, respectively.[15] The IS value is somewhat smaller than the corresponding value observed for I under identical conditions (IS, 0.494; ΔE_Q, 1.095 mm/s; 125 K) and is consistent with the higher formal oxidation state for the iron atoms in III. The appearance of only one Fe site in the spectra suggests electron delocalization not unlike the one found in I and the Fe_4S_4 centers. The magnetic moment of III measured in solution by NMR ($\mu_{eff}{}^{corr}$ 3.1 μ_B at 296 K) suggests magnetic coupling between the iron atoms at this temperature. The absence of an EPR signal and the insensitivity of the Mössbauer spectra to a weak magnetic field at 7 K indicate that this coupling results in a $S = 0$ ground magnetic state.

The oxidative transformation of $(Fe_4S_4Cl_4)^{2-}$ to III should be contrasted with the oxidative transformation of the Fe_4S_4 centers to Fe_3S_4 centers in certain ferredoxins. The apparent structural difference of the oxidation products in the two systems may reflect the ability of the protein substrate to "capture" unstable intermediates and prevent subsequent rearrangements or higher order coupling reactions.

The facile reversible reduction of III at low potential ($E_{1/2}$, 0.32 V, in CH_2Cl_2 vs. SCE) reveals a new Fe/S redox couple and introduces the Fe_6S_6 core as a viable candidate for future consideration in the biochemistry of "unconventional" and perhaps hitherto unknown Fe/S proteins.

Acknowledgment. This research was supported by a grant from the National Institutes of Health (No. GM-26671). X-ray equipment used in this research was obtained in part by a Grant (CHE-8109065) from the National Science Foundation.

Supplementary Material Available: Tables of structure factors and positional and thermal parameters (17 pages). Ordering information is given on any current masthead page.

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(14) Crystal and refinement data for $(Ph_4P)_2(Fe_6S_6Cl_6)$ (III): $a = 13.454$ (9) Å, $b = 13.528$ (8) Å, $c = 19.211$ (11) Å, $\alpha = 74.31$ (5)°, $\beta = 70.27$ (5)°, $\gamma = 61.51$ (4)°; space group $P\bar{1}$, $Z = 2$; $d_{calcd} = 1.65$, $d_{obsd} = 1.62$, $\mu = 22.8$ cm^{-1}, $2\theta_{max} = 41°$ (Mo, $\lambda(K\alpha)$, 0.71069 Å); Reflections collected 5824; unique reflections 5467 used in refinement $F_o{}^2 > 3\sigma(F_o{}^2)$, 2973; parameters 373; final $R = 0.06$.

(15) The IS and ΔE_Q values at 150 and 175 K are 0.41 and 0.66 mm/s and 0.44 and 0.72 mm/s, respectively. At 4.2 K the Mössbauer spectra of both $[Fe_6S_6Cl_6]^{2-}$ and $[Fe_6S_6Br_6]^{2-}$ show three quadrupole doublets in an approximate 1:1:1 ratio. The origin of this *reversible* change in the Mössbauer spectra at low temperatures presently is under study.

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cis-$(NH_3)_2Pt^{IV}$ Complexes of Uracil through Cl_2 Treatment of a Pt(II) Complex: Oxidative Addition to the Metal and Modification (Cl Substitution, HOCl Addition) of the Nucleobase

Gerhard Müller, Jürgen Riede, Rut Beyerle-Pfnür, and Bernhard Lippert*

Anorganisch-Chemisches Institut
Technische Universität München, 8046 Garching, FRG

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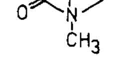
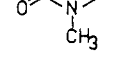
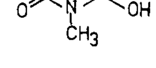
The role of metal ions in nucleic acid chemistry has evoked considerable interest in metal binding properties of nucleobases.[1] The coordination chemistry of the naturally occurring pyrimidine nucleobases uracil and thymine is, with metal coordination through the N(3) site, dominated by low coordination numbers of the metals bound, e.g., 2 for Ag[2] and Hg[3] and 4 for Pt.[4] Only one example with a five-coordinate metal, Cd,[5] has been structurally characterized as yet, but not a single example of a six-coordinate metal bound to N(3). The expected interference of the exocyclic oxygens at either side of N(3) with other ligands around the metal seems to be responsible for this lack.[6] We herewith wish to report the first examples of 1-methyluracil derivatives containing an octahedrally coordinated metal, Pt(IV), bound through N(3), *mer*-$(NH_3)_2PtCl_3L$ with $L = C_5H_5N_2O_2$ (**2**), $C_5H_4N_2O_2Cl$ (**3**), and $C_5H_5N_2O_3Cl_2$ (**4**).



2



3



4

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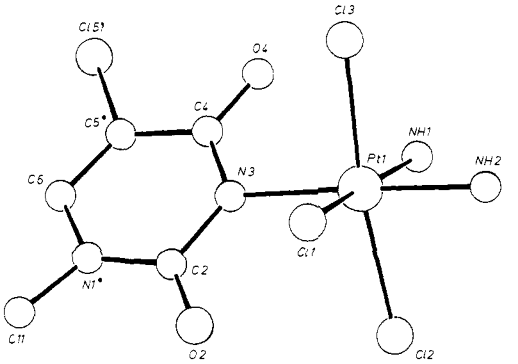

Figure 1. Molecular structure of one of two crystallographically independent molecules of 3. The heterocyclic ring is disordered about the N(3)–C(6) axis, thus making C(2)/C(4), O(2)/O(4), and N(1)*/C(5)* indistinguishable. The disorder could be resolved for the C and Cl atoms at N(1)* and C(5)*. Only one alternative is shown.

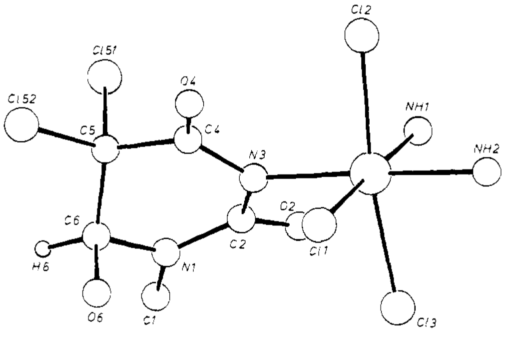

Figure 2. Molecular structure of 4.

Formation of **3** and **4** was unexpected since the way of preparation—oxidative addition of Cl_2 to a Pt(II) complex—was a general route of preparing *trans*-dichloro complexes of Pt(IV),[7] and similar chlorination reactions of ligands, except for Pt^{IV}–NH_3 groups,[8] appear not to have been reported before.

2 was obtained as follows: 405 mg of *cis*-$(NH_3)_2Pt(1\text{-}MeU)Cl{\cdot}H_2O$ (**1**)[9] (1-MeU = 1-methyluracil anion, $C_5H_5N_2O_2$) was dissolved in 35 mL of H_2O and 15 mL of freshly prepared chlorine water was added. Concentration of the yellow solution (pH 2.3) after 24 h at 22 °C to 10 mL and slow evaporation (8 days at 3 °C) gave lemon-yellow, transparent crystals of **2** which, at a later stage, were contaminated with small amounts of **1**, yield 340 mg.[10,11] **3** was obtained after Cl_2 gas had been bubbled through a solution of 204 mg of **1** in 40 mL of H_2O for 40 s, subsequent concentration of the orange-yellow solution (pH 1.3) to 5 mL and evaporation at 22 °C. Within 24 h, 180 mg of **3** (yellow, transparent cubes) was collected on a filter.[11,12] On further evaporation, pale yellow crystal plates of **4** were isolated in low yield (10 mg). Alternatively, **4** was prepared in good yield from isolated **3** (100 mg suspended in 10 mL of H_2O) on addition of Cl_2 gas (1.5 min) and evaporation at 22 °C.[11,13]

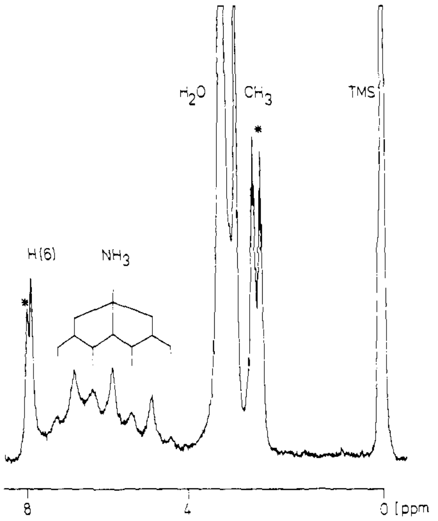

Figure 3. ^1H NMR spectrum of **3** in DMF-d_7. The NH_3 resonances are split due to ^{14}N–^1H coupling (three center lines) and further due to ^{195}Pt–^1H coupling (satellites). Solvent signals are indicated by an asterisk.

The molecular structures[14,15] of **3** and **4** have been determined by X-ray crystallography (Figures 1 and 2). In both compounds the uracil ring is coordinated through N(3) to a *cis*-diammineplatinum(IV) residue which completes its coordination sphere with three meridional Cl ligands. The geometry of the Pt is roughly octahedral. The Pt–NH_3 (2.05 (1)–2.08 (2) Å) and Pt–Cl distances (2.310 (6)–2.334 (3) Å) compare well with similar complexes of Pt(IV),[16] but the Pt–N(3) bonds to the uracil (2.14 (2) and 2.09 (2) Å in **3**, 2.08 (1) Å in **4**) show a trend to somewhat larger values as compared to related complexes of *cis*-$(NH_3)_2Pt^{II}$.[4,17]

Apart from obvious differences in the geometries of the two rings in **3** and **4**, the basic structural features of the two compounds are very similar. They are dictated by the steric restraints imposed by the three meridional Cl ligands and the two exocyclic oxygens in ortho positions to the Pt coordination site. The mutual repulsion between O(4) and O(2) of the ring and the chloro ligands around the Pt as well as a presumed hydrogen bonding attraction between one of the two oxygens and the ammonia ligands in the $PtCl_3$ plane lock the ring in a position such that its plane (in **4** the plane N(3),C(4),C(2)) roughly bisects the angle between two Cl ligands. As a consequence, dihedral angles between the $(NH_3)_2PtClN(3)$ plane and the ring plane are substantially smaller than in related complexes of Pt(II), 41.0° and 41.4° in **3** and 52.7° in **4**.[4,17] Nonbonding distances between the exocyclic oxygens of the rings and the Cl atoms at the Pt are short in both compounds and have to be considered van der Waals contacts (e.g., Cl(1)–O(4) 3.13 (1) Å; Cl(2)–O(4) 3.01 (1) Å; Cl(3)–O(2) 3.06 (1) Å in **4**, 2.97 (2)–3.17 (2) Å in **3**). The intramolecular hydrogen bond between

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(7) See, e.g.: Kauffman, G. B. *Inorg. Synth.* **1963**, *7*, 237.

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(10) Elemental analysis of **2**. Anal. Calcd for $Pt(NH_3)_2(C_5H_5N_2O_2)Cl_3{\cdot}H_2O$: C, 12.55; H, 2.74; Pt, 40.76. Found: C, 12.66; H, 2.72; Pt, 40.1.

(11) ^1H NMR chemical shifts of **2**, **3**, and **4** (DMF-d_7) are given in the supplementary material.

(12) Elemental Analysis of **3**. Anal. Calcd for $Pt(NH_3)_2(C_5H_4N_2O_2Cl){\cdot}2H_2O$: C, 11.31; H, 2.66; Cl, 26.70; Pt, 36.73. Found: C, 11.48; H, 2.58; Cl, 26.96; Pt, 36.0.

(13) Elemental analysis of **4**. Anal. Calcd for $Pt(NH_3)_2(C_5H_5N_2O_3Cl_2){\cdot}2H_2O$: C, 10.29; H, 2.60; N, 9.60; Cl, 30.37. Found: C, 10.50; H, 2.50; N, 9.62; Cl, 30.55. When kept in air, crystals of **4** lose water of crystallization and are no longer transparent.

(14) **3**: Monoclinic, space group $P2_1/c$, $a = 13.468$ (4) Å, $b = 11.345$ (3) Å, $c = 18.932$ (5) Å, $\beta = 105.54$ (2)°, $V = 2786.96$ Å^3, $d_{calcd} = 2.531$ g cm^{-3} for $Z = 8$, μ(Mo Kα) = 109.58 cm^{-1}; 4362 unique reflections (MoKα, $\lambda = 0.71069$ Å, ω-scan, $1° \leq \vartheta \leq 24°$, $T = -35$ °C, Syntex P2$_1$); empirical absorption correction; solution by heavy-atom method; $R = 0.06$, $R_w = 0.07$, unit weights, for 200 parameters and 3605 reflections with $F \geq 4.0\sigma(F)$ (Pt, Cl atoms anisotropic, all others isotropic, H atoms not included, SHELX 76); $\Delta\rho_{max} = 2.9$ e Å^{-3} with maxima near Pt and much smaller values elsewhere.

(15) **4**: Monoclinic, space group $P2_1/c$, $a = 9.484$ (5) Å, $b = 11.426$ (5) Å, $c = 15.469$ (7) Å, $\beta = 106.69$ (3)°, $V = 1605.67$ Å^3, $d_{calcd} = 2.414$ g cm^{-3} for $Z = 4$, μ(Mo Kα) = 96.89 cm^{-1}; 2713 unique reflections (Mo Kα, ω-scan, $1 \leq \vartheta \leq 25°$, $T = -40$ °C); empirical absorption correction; Patterson methods; $R = 0.056$, $R_w = 0.059$, $w = k/\sigma^2(F_o)$, $k = 3.3$ in last cycle (non-H atoms anisotropic, H atoms at C(6)/C(1) fixed, ammine hydrogens not included) 171 parameters, 2279 reflections with $F \geq 4.0\sigma(F)$; $\Delta\rho_{max} = 3.07$ e Å^{-3}.

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one of the exocyclic oxygens and NH_3 is normal (2.71 (3) and 2.62 (3) Å between O(4)/O(41) and NH(1)/NH(11) in **3**, 2.71 (2) Å between O(2) and NH(1) in **4**). The steric crowding around Pt causes deviations from strict octahedral geometry about the Pt such as to relieve the repulsion between the O atoms and the Cl ligands, e.g., Cl(3)–Pt–Cl(2) 172.3 (1)°, N(3)–Pt–Cl(2) 95.1 (3)°, Cl(2)–Pt–NH(2) 85.7 (4)° in **4**.

Unlike the ^1H NMR spectra of ammine complexes of Pt(II), which only exhibit $^{195}Pt-^1H$ coupling, the NH_3 resonances of **2–4** show both $^{14}N-^1H$ ($J = 53$ Hz) and $^{195}Pt-^1H$ coupling ($J \simeq 50$ Hz), leading to a characteristic seven-line pattern in the 5–7 ppm region (Figure 3).[18]

In summary, it has been shown that in aqueous solution Cl_2 not only oxidizes Pt(II) in *cis*-$(NH_3)_2Pt$(1-MeU)Cl to the corresponding Pt(IV) complex but at the same time causes substitution of H(5) of the 1-MeU ligand by Cl and subsequently addition of HOCl to the 5.6 double bond of the 5-chloro-1-methyluracil ligand. The isolated complexes are the first examples of pyrimidine-2,4-dione nucleobases containing a hexacoordinated metal bound through N(3).

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Technische Universität München for financial support and Degussa for a loan of K_2PtCl_4.

Supplementary Material Available: Additional crystal structure data, atomic positional parameters for **3** and **4**, and ^1H NMR data of **2–4** (12 pages). Ordering information is given on any current masthead page.

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(18) The asymmetry of the seven-line pattern of the NH_3 resonances most likely arises from the involvement of one of the six ammine protons in hydrogen bonding, rather than from the geometric inequivalence of the two NH_3 groups, since most *cis*-$(NH_3)_2PtXY$ complexes show only one set of NH_3 resonances. Hydrogen bonding is expected to shift the resonance of the proton involved to lower field. In *cis*-$(NH_3)_2PtCl_4$ the seven-line pattern is completely regular, 1:4:2:4:2:4:1.

Exceptionally Facile Reduction of Acyclic and Alicyclic Carboxylic Acids to Aldehydes by Thexylchloroborane–Dimethyl Sulfide

Herbert C. Brown,* Jin Soon Cha,[1] Behrooz Nazer,[2] and Nung Min Yoon[3]

Richard B. Wetherill Laboratory, Purdue University
West Lafayette, Indiana 47907

Received July 2, 1984

The discovery of an exceptionally facile reduction of acyclic and alicyclic carboxylic acids to alcohols by borane–tetrahydrofuran revolutionized the reduction of this ordinarily very resistant group for synthetic work.[4] We wish now to report an equally facile reduction of such carboxylic acids to aldehydes by thexylchloroborane–dimethyl sulfide.[5]

Numerous reagents have been proposed to achieve this objective.[6] Unfortunately, the ideal reagent has not yet been described.

Table I. Yields of Aldehydes in the Reduction of Representative Carboxylic Acids with Thexylchloroborane–Dimethyl Sulfide in Methylene Chloride at Room Temperature[a]

acid	yield of aldehyde, % by analysis with (2,4-dinitrophenyl)hydrazine	yield of aldehyde, % by isolation using sodium bisulfite adduct[b]
hexanoic	99	83[c]
decanoic	97	89
stearic	98	92
pivalic	98[d]	71[c,d]
cyclohexanecarboxylic	91	80
cyclopentanecarboxylic	89	82
1-adamantanecarboxylic	99	88
diphenylacetic	91	83
1,10-decanedicarboxylic	97	93
6-bromohexanoic	98	86
adipic acid monoethyl ester	93–100[e]	81
benzoic	59	47
p-methoxybenzoic	51	46
p-nitrobenzoic	86	71
m-cyanobenzoic	83	67

[a] Reacted with 10% excess reagent (2.2 equiv for monocarboxylic and 4.4 equiv for dicarboxylic acid) for 15 min with aliphatic and for 24 h with aromatic carboxylic acids, both at room temperature after the hydrogen evolution at 0 °C. [b] Yields are based on the analytically pure aldehydes isolated after evaporation of solvent, following treatment of the adduct with formaldehyde. [c] Yields on distillation of the regenerated product. [d] Reacted for 3 h; 62% for 15 min. [e] A mixture of the (2,4-dinitrophenyl)hydrazones of 5-carboethoxypentanal and 5-carboxypentanal.

At one time the reaction of thexylborane with carboxylic acids appeared promising.[6b] However, the reaction was slow, requiring refluxing in THF for 36 h. Under these conditions, many other groups undergo reduction.

In the course of exploring the reducing action of thexylchloroborane,[6] we observed that acyclic and alicyclic carboxylic acids are reduced to aldehydes in high yields in a matter of minutes at 25 °C. This intrigued us. A simple reduction of carboxylic acids to aldehydes has long escaped us. We have utilized the reduction of acid chlorides by lithium tri-*tert*-butoxyaluminum hydride[7] (LTBA) and the reduction of nitriles[8] and dimethylamides[9] by "lithium diethoxyaluminum hydride", as well as the reduction of acylaziridines by lithium aluminum hydride.[10] Finally, the reduction of carboxylic acid by thexylborane, referred to above, had been explored.[6b] But a really clean reduction had escaped us.

The reagent, thexylchloroborane–dimethyl sulfide, is readily synthesized by treating thexylborane–dimethyl sulfide with 1 equiv of hydrogen chloride[5a] or by hydroborating 2,3-dimethyl-2-butene with monochloroborane–dimethyl sulfide in methylene chloride.[5c] We discovered that this new reaction, based on this reagent, provides an apparently ideal procedure. It reduces aliphatic carboxylic acids to aldehydes in approximately 15 min at room temperature in yields of 93–99%. Alicyclic derivatives, such as cyclohexanecarboxylic acid, cyclopentanecarboxylic acid, and

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(1) Postdoctoral research associate on a grant supplied by the U.S. Army Research Office.

(2) Present address: Dow Chemical Company, Midland, MI.

(3) On sabbatical leave, 1983–1984, from Sogang University, Seoul, Korea.

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