coplanar and parallel. This is now known to result in weak exchange between the metals.[20,21]

Concluding Remarks

The results of the present study have once again illustrated that thiocyanate anions are, especially with Cu^{2+}, versatile ambidentate ligands. The two distortion isomers (α and β) of $[Cu(NCS)_2(dmtp)_2]_2$ are the first examples, to the best of our knowledge, of this isomerism in dinuclear Cu(II) compounds. The magnetic exchange coupling between the Cu^{2+} ions in the dimers is very small in each isomer and could be deduced only spectroscopically from the ESR data. Even ESR spectra are sometimes nonconclusive for the presence of dimers, as recently shown by Hatfield,[22] therefore, we cannot completely exclude that the hydrate $Cu(NCS)_2(dmtp)_2H_2O$ is oligomeric, despite the fact that far-infrared spectra point toward coordinated water in a mononuclear species.

Acknowledgment. The authors are indebted to B. v. d. Griendt and S. Gorter for assistance with the magnetic susceptibility measurements and X-ray data collection.

Registry No. $Cu(NCS)_2(dmtp)_2H_2O$, 90991-02-9; α-$[Cu(NCS)_2(dmtp)_2]_2$, 91050-44-1; β-$[Cu(NCS)_2(dmtp)_2]_2$, 90991-03-0.

Supplementary Material Available: Listings of anisotropic thermal parameters and observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Formation, Crystal Structure, and EPR Spectroscopic Properties of a Heteronuclear (Pt_2, Cu) Mixed-Nucleobase (1-Methylcytosine, 1-Methyluracil) Complex: Bis[(μ-1-methyluracilato-N^3,O^4)(μ-1-methylcytosine-N^3,O^2)-*cis*-diammineplatinum(II)]copper(II) Tetranitrate-6-Water

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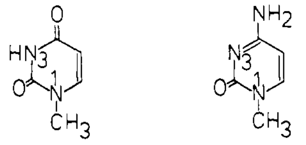
The mixed-nucleobase complex *cis*-diammine(1-methylcytosine-N^3)(1-methyluracilato-N^3)platinum(II) nitrate, $[Pt(NH_3)_2(C_5H_7N_3O)(C_5H_5N_2O_2)]NO_3\cdot2H_2O$ (**1**), has been prepared and characterized by using ^1H NMR, IR, and Raman spectroscopy. NMR spectra show that in acidic medium the 1-MeU ligand becomes protonated ($pK_a \simeq 0.9$) and in a slow secondary reaction releases neutral 1-methyluracil. The pK_a of the NH_2 (N4) group of N3-platinated 1-methylcytosine in **1** has been estimated to be ≥ 14. In the presence of Cu(II), **1** forms a trinuclear complex **2**, bis[(μ-1-methyluracilato-N^3,O^4)(μ-1-methylcytosine-N^3,O^2)-*cis*-diammineplatinum(II)]copper(II) tetranitrate–6-water, $[Pt(NH_3)_2(C_5H_5N_2O_2)(C_5H_7N_3O)Cu(C_5H_7N_3O)(C_5H_5N_2O_2)(NH_3)_2Pt](NO_3)_4\cdot6H_2O$. The crystal structure of this heteronuclear complex has been determined. The compound crystallizes in space group $P\bar{1}$, with cell dimensions $a = 11.522$ (6) Å, $b = 10.924$ (4) Å, $c = 10.736$ (2) Å, $\alpha = 91.51$ (3)°, $\beta = 109.08$ (3)°, $\gamma = 114.43$ (3)°, and $Z = 1$. The structure was refined to $R = 0.051$ and $R_w = 0.054$ on the basis of 2603 reflections. Both Pt atoms are bound to N3 of 1-methyluracil and N3 of 1-methylcytosine, respectively, while Cu binds to O4 of uracil and O2 of cytosine in pairs. All three metals have square-planar coordination spheres, with Cu sitting in the inversion center of the Pt_2,Cu unit. The Pt–Cu distances within the cation are 2.681 (1) Å. Cu–O distances to 1-methyluracil (1.931 (12) Å) and 1-methylcytosine (1.988 (9) Å) do not differ greatly. EPR spectra, at X- and Q-band frequencies, are consistent with a tetragonally elongated ligand field about the Cu^{2+} ion in **2** and also in the related complexes *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Cu(1\text{-}MeU)_2Pt(NH_3)_2]^{2+}$. The spectra are compared with those of the dinuclear complex *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Cu(H_2O)_2]^{2+}$ for which a significant dipolar coupling between the Cu^{2+} ions in a centrosymmetrically related pair of cations in the unit cell is observed.

Introduction

The ligating properties of the individual pyrimidine nucleobases 1-methylcytosine and 1-methyluracil and their respective analogues toward metal ions have been extensively studied over the past years,[2] with the purpose of better understanding the more complex reactions of metal ions with nucleic acids (Chart I). As a result, it has become evident that there is a versatility in the binding patterns of these two nucleobases, depending on pH and the metals present. It has also been demonstrated that different metals may be bound simultaneously to the deprotonated 1-methyluracil ligand, 1-MeU, or its 1-methylthymine analogue, e.g. *cis*-$(NH_3)_2Pt^{II}$, Ag(I), Mn(II), Cu(II), and Na(I)[3] or CH_3Hg^{II} and Na(I),[4]

Chart I



1-Methyluracil
1-MeUH

1-Methylcytosine
1-MeC

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respectively, with binding sites being N3, O4, and O2. With 1-methylcytosine, 1-MeC, metal coordination to more than one site has been observed as well, e.g. N3 and the deprotonated amino group N4 by *cis*-(NH$_3$)$_2$Pt^{II},[5] CH$_3$Hg^{II},[6] and enPd^{II}[7] or N3 and O2 as with Ag(I),[8] Cu(II),[9] Zn(II),[10] Cd(II),[11] Hg(II),[12] and Ca(II).[13] While in N3,N4-bridged complexes the respective metal–nitrogen bonds are of comparable length, with N3,O2-bridged complexes the metal–O2 interactions usually are weaker than those between the metal and N3. This suggests that metal coordination to N3 of cytosine effectively reduces the available negative electrostatic potential at O2.[14] Thus, the situation for N,O bridging in the 1-MeC system contrasts with that observed in the 1-MeU system, where metal binding to N3 of the anionic uracil ligand facilitates binding of additional metals to the adjacent exocyclic oxygens. This assumption is further supported by our findings that *cis*-[(NH$_3$)$_2$Pt(1-MeC)H$_2$O]$^{2+}$, rather than forming a N3,O2-bridged head–tail dimer, crystallizes from aqueous solution as a monomer with a coordinated aquo group[15] and that, unlike in the uracil and thymine system, there is no series of easily accessible heteronuclear complexes derived from *cis*-[(NH$_3$)$_2$Pt(1-MeC)$_2$]$^{2+}$ with Pt coordinated to N3 of the neutral 1-MeC.

In an attempt to encourage metal–O2 coordination at an N3-platinated 1-MeC through preformation of a sterically favorable environment by means of a second ligand, we have studied the ability of *cis*-[(NH$_3$)$_2$Pt(1-MeU)(1-MeC)]$^+$ to bind other metal ions. The present paper describes the preparation, crystal structure, and the EPR spectrum of a complex containing two different nucleobases, 1-MeC and 1-MeU, and two different metal ions, Pt(II) and Cu(II), simultaneously linked together. The parent compound of this heteronuclear complex, *cis*-[(NH$_3$)$_2$Pt(1-MeU)(1-MeC)]$^+$ is of interest because it represents a model for a hypothetical crosslink of the antitumor agent *cis*-(NH$_3$)$_2$PtCl$_2$ with the N3 sites of a cytosine and a thymine base in the core of a DNA helix.[16] Formation of a mixed uridine–cytidine complex of enPd^{II} has recently also been reported by Häring and Martin,[7] who showed that it is more stable than expected statistically by comparison with the individual 2:1 complexes.

Experimental Section

Compounds. *cis*-[(NH$_3$)$_2$Pt(1-MeU)(1-MeC)]NO$_3$·2H$_2$O (1) was prepared by the method used for the corresponding 1-methylthymine complex[16] from *cis*-(NH$_3$)$_2$Pt(1-MeU)Cl,[17] which had been obtained from cis-(NH$_3$)$_2$Pt(1-MeU)$_2$[3a] on HCl treatment. *cis*-[(NH$_3$)$_2$Pt(1-MeU)Cl]·H$_2$O (1.5 mmol) was treated in 25 mL of H$_2$O with 1.5 mmol of AgNO$_3$ and 1.5 mmol of 1-MeC at 40 °C. After 24 h AgCl was filtered off and the solution concentrated to 8 mL and allowed to evaporate on air. An 840-mg sample (90%) of **1** was collected on a filter and recrystallized from H$_2$O: colorless crystals. Anal. Calcd for PtC$_{10}$H$_{22}$N$_8$O$_8$: C, 20.80; H, 3.85; N, 19.41; Pt, 33.78. Found: C, 21.06; H, 3.74; N, 19.59; Pt, 34.1.

***cis*-[(NH$_3$)$_2$(1-MeU)(1-MeC)Pt]$_2$Cu(NO$_3$)$_4$·6H$_2$O (2)** was obtained on cocrystallization of **1** and Cu(NO$_3$)$_2$·3H$_2$O (0.1 mmol each in 2 mL of H$_2$O) at 3 °C. From the green solution (pH 4) green cubes of the title compound were isolated in 60–70% yield on slow evaporation and briefly dried in air. Extensive drying has to be avoided since it causes fracture of the crystals. Anal. Calcd for Pt$_2$CuC$_{20}$H$_{48}$N$_{18}$O$_{24}$ (hexahydrate): C, 17.42; H, 3.52; N, 18.29; O, 27.85; Cu, 4.61. Found: C, 17.15; H, 3.70; N, 17.94; O, 28.68; Cu, 4.60. Formulation as heptahydrate fits the analysis data better for all elements determined except Cu. A thermogravimetric measurement indicated a 9% loss of weight between 30 and 115 °C with no further change until decomposition of the compound. This value also favors formulation as a heptahydrate. Crystallographically only six H$_2$O molecules were localized, but we cannot exclude the possibility of a disordered seventh water molecule present.

***cis*-[(NH$_3$)$_2$Pt(1-MeU)$_2$Cu(1-MeU)$_2$Pt(NH$_3$)$_2$]X$_2$ (X$_2$ = SO$_4$·12H$_2$O (3), X = NO$_3$·6H$_2$O (4)) and *cis*-[(NH$_3$)$_2$Pt(1-MeU)$_2$Cu(H$_2$O)$_2$]SO$_4$·4.5H$_2$O (5)** were prepared as previously reported.[3a]

Spectra. ^{1}H NMR spectra were recorded on a JEOL JNM-FX 60 Fourier transform spectrometer as previously described.[3a] Concentrations of **1** in D$_2$O were 0.1 M. The pD was varied by addition of NaOD and CF$_3$COOD, respectively, and pD values were obtained by adding 0.4 to the pH meter reading. IR spectra were recorded on a Perkin-Elmer 580 grating spectrometer as KBr pellets and Nujol mulls (CsI). Raman spectra of **1** were obtained with a Coderg PH 1 with krypton-laser excitation (647.1 nm; 100 mW for solid sample, 700 mW for solution) and calibrated against indene. The thermogravimetric measurement was performed with a Perkin-Elmer TGS-2 system under Ar atmosphere at a rate of 10 °C min^{-1}. EPR spectra were measured at room temperature on polycrystalline samples. X-Band measurements were made on a Varian E-12 spectrometer. The Q-band spectrometer comprised a Varian 36-GHz microwave bridge and a Newport 12-in. type F magnet powered by a C905 rotary generator and post stabilizer.

Crystallography. A crystal fragment of compound **2** (dimensions approximately 0.2, 0.2, 0.3 mm) was chosen for the X-ray measurements. Crystal data were taken at room temperature on a Philips PW-1100 single-crystal diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The following unit cell dimensions were obtained for the triclinic crystals from 2θ values for 20 reflections, centered on the diffractometer: a = 11.522 (6) Å, b = 10.924 (4) Å, c = 10.736 (2) Å, α = 91.51 (3)°, β = 109.08 (3)°, γ = 114.43 (3)°, d_{obsd} = 2.01 g/cm^3, d_{calcd} = 1.986 g/cm^3, Z = 1, formula weight 1366.3. The space group $P\bar{1}$ was confirmed by the successful solution and refinement in this space group.

Intensity data were collected by using a θ–2θ scan technique at a 2θ scan rate of 3.6°/min and a total scan width of 1.2°. Stationary background counts (B_1, B_2) of 5 s each were taken at the limits of the scan. A total of 2980 independent reflections were measured out to 2θ = 44°. The reflection intensities were corrected for absorption by an empirical method using the program of Walker and Stuart[18] (μ = 64 cm^{-1}) and for Lorentz and polarization effects. The set of 2603 reflections with $F_o \geq 2\sigma(F_o)$ was used in the subsequent calculations.

The coordinates of the platinum atom were found in a three-dimensional Patterson synthesis. The copper atom is situated on a inversion center at 0,0,0. The other non-hydrogen atoms were located by subsequent ΔF syntheses. Hydrogen atoms were ignored at all stages. The metal atoms were refined with anisotropic and the remaining atoms with isotropic temperature factors. Scattering factors for neutral atoms were taken from Cromer and Mann.[19] Anomalous dispersion corrections were applied.[20] R = 0.051, R_w = 0.054 ($R_w = \sum(||F_o| - |F_c||)w^{1/2}/\sum|F_o|w^{1/2}$ with $w = 1.67/(\sigma^2(F) + 0.0012F^2)$.

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Table I. Positional Parameters and Temperature Factors (Å^2) for the Pt_2,Cu Complex **2**[a]

atom	*x*	*y*	*z*	*U*
Pt	0.0915 (1)	0.0941 (1)	0.2638 (1)	0.035 (1)
Cu	0.0 (0)	0.0 (0)	0.0 (0)	0.042 (2)
N1	−0.0984 (11)	−0.0135 (11)	0.2797 (11)	0.049 (3)
N2	0.0600 (12)	0.2672 (11)	0.2507 (11)	0.051 (3)
N1c	0.4113 (12)	0.2890 (12)	0.1184 (11)	0.053 (3)
C1c′	0.4187 (19)	0.2933 (19)	−0.0145 (19)	0.081 (5)
C2c	0.2922 (13)	0.2048 (12)	0.1291 (12)	0.041 (3)
O2c′	0.1919 (10)	0.1281 (9)	0.0250 (10)	0.056 (2)
N3c	0.2782 (10)	0.2028 (10)	0.2509 (10)	0.038 (2)
C4c	0.3904 (14)	0.2793 (13)	0.3650 (13)	0.047 (3)
N4c′	0.3778 (13)	0.2749 (13)	0.4799 (13)	0.065 (3)
C5c	0.5163 (15)	0.3696 (15)	0.3522 (15)	0.057 (4)
C6c	0.5210 (15)	0.3671 (15)	0.2321 (15)	0.059 (4)
N1u	0.1782 (13)	−0.2206 (12)	0.4224 (12)	0.061 (3)
C1u′	0.2207 (20)	−0.2496 (19)	0.5569 (20)	0.084 (5)
C2u′	0.1704 (13)	−0.0952 (13)	0.4071 (13)	0.045 (3)
O2u′	0.2049 (11)	−0.0106 (10)	0.5048 (10)	0.064 (3)
N3u	0.1220 (10)	−0.0774 (10)	0.2798 (10)	0.042 (3)
C4u	0.0933 (13)	−0.1648 (12)	0.1700 (13)	0.041 (3)
O4u′	0.0500 (10)	−0.1438 (10)	0.0559 (10)	0.056 (2)
C5u	0.1087 (14)	−0.2857 (14)	0.1908 (14)	0.054 (4)
C6u	0.1460 (16)	−0.3119 (16)	0.3134 (16)	0.063 (4)
N40	0.3306 (16)	0.5573 (16)	0.2107 (16)	0.078 (4)
O40	0.3334 (13)	0.5328 (12)	0.3225 (13)	0.082 (3)
O41	0.2398 (15)	0.4827 (14)	0.1112 (14)	0.102 (4)
O42	0.4238 (21)	0.6687 (19)	0.2052 (19)	0.148 (6)
N50	0.1403 (14)	0.3339 (14)	0.6129 (14)	0.068 (4)
O50	0.1004 (13)	0.2242 (13)	0.5418 (13)	0.090 (4)
O51	0.1801 (14)	0.3458 (14)	0.7319 (14)	0.095 (4)
O52	0.1406 (17)	0.4250 (17)	0.5482 (17)	0.126 (5)
O60	−0.2842 (15)	0.1194 (14)	0.1119 (14)	0.103 (4)
O61	0.1939 (16)	0.6031 (16)	0.8640 (16)	0.117 (5)
O62	0.4499 (24)	0.0016 (23)	0.1614 (23)	0.181 (8)

[a] For Pt and Cu the equivalent isotropic temperature factors are given.

The highest peak in the final difference Fourier map was 1.67 e/Å^3 (1.07 Å away from Pt and therefore of no chemical significance). The atomic parameters are listed in Table I. For Pt and Cu the equivalent isotropic temperature factors were calculated from the U_{ij} values by $U_{eq} = {}^1/_3\sum U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$ (U_{ij} in Å^2). The SHELX program package[21] was used in this structure analysis.

There is no straightforward crystallographic differentiation between 1-MeU and 1-MeC possible. The assignment has been made on the basis of chemical arguments. If 1-MeU and 1-MeC are interchanged, one is confronted with the situation that 1-MeC coordinates through its NH_2 group in the 4-position to Cu, while Cu binds to 1-MeU via O2. All presently available evidence tells that coordination at the amino group of cytosine occurs only under deprotonation of it[5-7] and that 1-MeU uses O2 as a donor site only if N3 and O4 are already blocked.[3b] Moreover, anionic 1-MeC disagrees with the presence of four nitrates, and the IR spectrum of **2** is consistent with N3,O4 bridging of 1-MeU, as evident from the positions of two characteristic ring modes at 505 and 630 cm^{-1}.

Results and Discussion

Characterization of *cis*-[$(NH_3)_2Pt(1\text{-}MeU)(1\text{-}MeC)]NO_3$ (1). The ^1H NMR spectrum of **1** in the low-field region is shown in Figure 1. Individual resonances are identified by comparison with related complexes of *cis*-$(NH_3)_2Pt^{II}$ and 1-MeU[3a,17] and 1-MeC, respectively.[16,22] Platinum binding to N3 of both pyrimidine bases is evident from four-bond coupling satellites of the H5 resonances due to the ^{195}Pt isotope. ^4J values are similar to previously observed ones: 1-MeU, 14.6 Hz; 1-MeC, 15.6 Hz. The pH dependence of the proton resonances has been monitored over the range 0–13 (Figure 2). In the pD range 0–2 a sigmoidal change in chemical shifts of the 1-MeU resonances is observed, indicating protonation of the 1-MeU ligand. The considerable broadening of the H5 and H6 resonances of 1-MeU below pD 1 (half-widths about three times those of the 1-MeC resonances and of 1-MeU resonances at higher pD) may be indicative of an equilibrium between O4- and O2-protonated species. The pK_a of the protonated 1-MeU ligand is 0.9 ± 0.05, which compares with −3.40 ± 0.12 for the nonplatinated 1-methyluracil cation[23] and 2.05 ± 0.05 for *cis*-[$(NH_3)_2Pt(1\text{-}MeT)(1\text{-}MeTH)]^+$.[24] The basicity of the exocyclic oxygen(s) of 1-MeU in **1** is thus higher by 4.2 pK units than in free 1-methyluracil. As evident from NMR, there is no deprotonation of either ligand below pD 13. With the NH_2 (N4) acidity of free 1-MeC being 16.7,[25] this

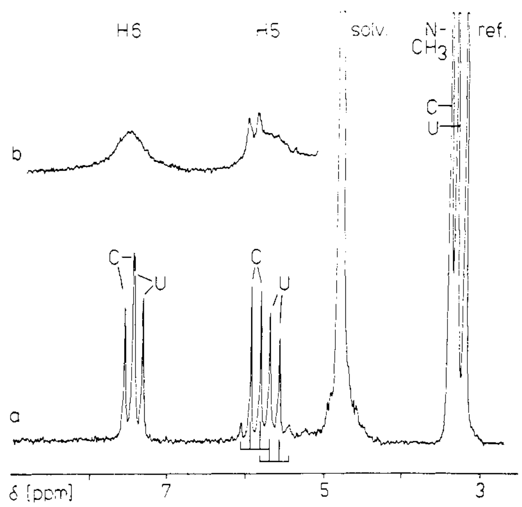

Figure 1. ^1H NMR spectra ($[N(Me)_4]^+$ internal reference): (a) *cis*-[$(NH_3)_2Pt(1\text{-}MeU)(1\text{-}MeC)]NO_3$ (**1**) (0.1 M Pt) in D_2O, pD 13 (spectrum at pD 3 is identical with an additional peak at 3.9 ppm due to unexchanged NH_3 protons); (b) after addition of $Cu(NO_3)_2$ (0.005 M) to a solution of **1** (0.2 M) at pD 6.

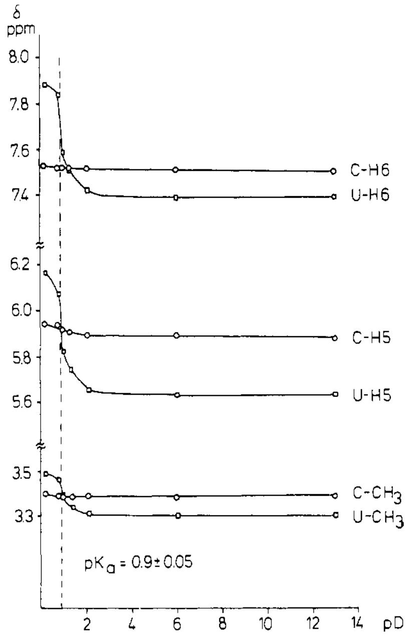

Figure 2. ^1H NMR chemical shifts of 1-MeU and 1-MeC resonances of *cis*-[$(NH_3)_2Pt(1\text{-}MeU)(1\text{-}MeC)]NO_3$ at pD values between 0.2 and 13. Only the 1-MeU resonances show a marked pH dependence in the low-pH region, indicating formation of [$(NH_3)_2Pt(1\text{-}MeUH)(1\text{-}MeC)]^{2+}$.

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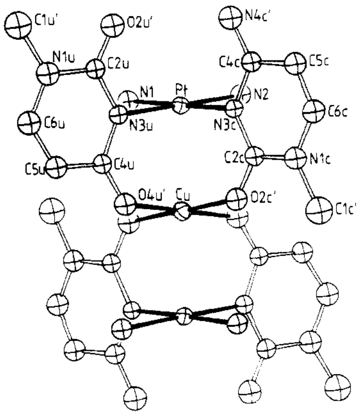

Figure 3. Molecular cation **2**, $[(NH_3)_2Pt(1\text{-}MeU)(1\text{-}MeC)Cu(1\text{-}MeC)(1\text{-}MeU)Pt(NH_3)_2]^{4+}$. In the numbering scheme 1-MeC atoms are indicated by c, and 1-MeU atoms, by u. Exocyclic atoms are labeled with a prime; e.g., N4c′ is the exocyclic N at the 4-position of 1-MeC. Only the atoms of the asymmetric unit are labeled. The Cu atom sits on an inversion center.

implies that Pt coordination to N3 certainly does not increase its acidity by more than 10^2 to 10^3. This tends to support our earlier interpretation that Pt binding to the exocyclic amino group occurs in a condensation reaction between NH_2 and a Pt–OH unit and not because the N3-platinated 1-MeC already is deprotonated.[5,15] Thus, the situation is similar to the reaction of MeHgOH and the amino groups of nucleobases, which leads to compounds containing methylmercury(II) bound to the deprotonated amino groups of adenine, guanine, and cytosine derivatives.[26]

The low-pD spectra of **1** confirm our earlier findings on the lability of the bond between Pt(II) and N3 of uracil and thymine in acidic medium.[16,24,27] At pD 0.2–0.8 displacement of the protonated uracilato ligand occurs on brief warming to 60 °C or slowly at room temperature according to

$$[(NH_3)_2Pt(1\text{-}MeU)(1\text{-}MeC)]^+ + H^+ \rightarrow [(NH_3)_2Pt(1\text{-}MeUH)(1\text{-}MeC)]^{2+} \xrightarrow{\Delta} [(NH_3)_2Pt(1\text{-}MeC)H_2O]^{2+} + 1\text{-}MeUH$$

The IR and Raman spectra of **1** are rather complex as expected. However, it is possible to discern a number of individual absorptions, since the spectra represent good superpositions of bands of N3-platinated 1-methyluracil and N3-platinated 1-methylcytosine previously reported by us.[17,22b] This refers in particular to the frequency range below 800 cm^{-1}. The Raman solution spectrum (H_2O, pH 5.6), for example, exhibits characteristic bands [794 vs (1-MeC, 1-MeU), 645 s (1-MeC, 1-MeU), 599 m (1-MeU), 581 m (1-MeC), 493 m (1-MeU), 478 m (1-MeC), 447 m (1-MeU), 427 cm^{-1} m (1-MeC)] besides the Pt–NH_3 stretch (ca. 524 cm^{-1}, s, b), which unambiguously confirm N3–platinum binding of both nucleobases.

Reaction with Cu(II) and Crystal Structure of the Pt_2,Cu Compound. Addition of small amounts of $Cu(NO_3)_2$ to a solution of **1** in D_2O leads to the expected paramagnetic broadening of the ^1H NMR resonances. It looks as if 1-MeU resonances are affected at lower concentrations of Cu(II) than are the 1-MeC resonances (cf. Figure 1b), which suggests that O4 of the 1-MeU ligand has an anchoring function for the copper ion, necessary to accomplish subsequent binding to O2 of 1-MeC. The cation of $[(NH_3)_2Pt(1\text{-}MeU)(1\text{-}MeC)Cu(1\text{-}MeC)(1\text{-}MeU)Pt(NH_3)_2](NO_3)_4\cdot 6H_2O$ is depicted in Figure 3, interatomic distances and selected angles are listed in Table II, and conformational parameters are given in Table III. The cation is trinuclear and centrosymmetric, containing two *cis*-$(NH_3)_2Pt^{II}$ moieties and one Cu(II). Both 1-MeU and 1-MeC are bound to Pt through N3, whereas Cu coordinates to the nucleobases through O4 of 1-MeU and O2 of 1-MeC. Thus, each nucleobase acts as a bridging, bidentate ligand. The Pt–Cu separation within the trinuclear cation is 2.681 (1) Å, significantly shorter than in the dinuclear *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Cu(H_2O)_2]^{2+}$ cation (2.765 (3) Å)[3a] and comparable to a related trinuclear complex containing two Pt(II), a Mn(II), and four 1-methylthyminato ligands (2.704 (1) Å).[28a] As indicated by the EPR results (vide infra), the rather short intermetallic distances within the cation of the title compound do not reflect a significant electronic interaction between Pt and Cu. We rather attribute it to geometric requirements caused by bite distances of the two heterocyclic ligands (2.258 (18) Å for 1-MeU and 2.278 (18) Å for 1-MeC) *and* the coordination geometries of Pt and Cu. If, for example, the Cu coordination sphere could undergo a distortion toward a tetrahedral environment, the intermetallic distances should lengthen in a similar way as is observed when Mn(II) in *cis*-$[(NH_3)_2Pt(1\text{-}MeT)_2Mn(1\text{-}MeT)_2Pt(NH_3)_2]^{2+}$ is replaced by the tetrahedrally coordinated Ag. There, the Pt–heterometal distance increases from 2.704 (1) to 2.866 (1) Å (average).[28b]

Table II. Interatomic Distances (Å) and Selected Angles (deg) for the Pt_2,Cu Complex **2**

Pt–Cu	2.681 (1)	N1u–C2u	1.419 (21)
Pt–N1	2.081 (12)	C2u–O2u′	1.218 (18)
Pt–N2	2.068 (14)	C2u–N3u	1.350 (17)
Pt–N3u	2.045 (13)	N3u–C4u	1.355 (18)
Pt–N3c	2.036 (11)	C4u–O4u′	1.230 (17)
Cu–O4u′	1.931 (12)	C4u–C5u	1.418 (23)
Cu–O2c′	1.988 (9)	C5u–C6u	1.324 (22)
N1c–C1c′	1.458 (25)	C6u–N1u	1.361 (22)
N1c–C2c	1.344 (18)	N40–O40	1.230 (22)
C2c–O2c′	1.262 (12)	N40–O41	1.190 (17)
C2c–N3c	1.369 (19)	N40–O42	1.265 (24)
N3c–C4c	1.373 (13)	N50–O50	1.224 (20)
C4c–N4c′	1.288 (22)	N50–O51	1.191 (21)
C4c–C5c	1.432 (21)	N50–O52	1.227 (25)
C5c–C6c	1.308 (24)	N3c···O2c′	2.278 (18)
C6c–N1c	1.364 (15)	N3u···O4u′	2.258 (18)
N1u–C1u′	1.454 (24)		
N1–Pt–N2	90.1 (5)	Pt–N3c–C2c	120.7 (8)
N1–Pt–N3c	178.8 (5)	N3c–C2c–O2c′	119.9 (12)
N1–Pt–N3u	89.2 (5)	C2c–O2c′–Cu	130.7 (9)
N2–Pt–N3c	89.0 (5)	C6u–N1u–C2u	120.6 (13)
N2–Pt–N3u	179.0 (5)	N1u–C2u–N3u	116.1 (11)
N3c–Pt–N3u	91.6 (5)	C2u–N3u–C4u	124.1 (11)
O4u′–Cu–O2c′	92.3 (4)	N3u–C4u–C5u	117.5 (12)
C6c–N1c–C2c	119.0 (12)	C4u–C5u–C6u	120.2 (13)
N1c–C2c–N3c	120.8 (11)	C5u–C6u–N1u	121.2 (15)
C2c–N3c–C4c	119.5 (11)	Pt–N3u–C4u	121.6 (9)
N3c–C4c–C5c	118.9 (12)	N3u–C4u–O4u′	121.7 (12)
C4c–C5c–C6c	117.7 (13)	C4u–O4u′–Cu	128.8 (9)
C5c–C6c–N1c	123.7 (15)		

Table III. Dihedral Angles (deg) between Various Planes[a]

Pt coord plane/ 1-MeC plane	87.4	Cu coord plane/ 1-MeC plane	101.2
Pt coord plane/ 1-MeU plane	97.2	Cu coord plane/ 1-MeU plane	96.6
1-MeU plane/ 1-MeC plane	102.4	Cu coord plane/ Pt coord plane	17.8

[a] Equations given in the supplementary material.

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Table IV. Close Contacts <3.30 Å and Angles (deg) at the Potential Hydrogen-Bond Donor Atoms[a]

N1-O60	3.18	O51-O61	3.03
N2-O40	3.11	O60-O62^1	2.84
N2-O41	3.20	O61-O41^2	2.98
N2-O50	3.09	N1-O50^3	3.03
N2-O52	3.24	N1-O2u'^{3}	3.00
N4c'-O2u'	3.00		
Pt-N1···O60	105.0	C4c-N4c'···O2u'	112.2
Pt-N2···O40	112.1	N50-O51···O61	111.6
Pt-N2···O41	113.6	O61···O41^2-N40^2	116.7
Pt-N2···O50	74.6	Pt-N1···O50^3	112.7
Pt-N2···O52	109.8	Pt-N1···O2u'^{3}	132.3

[a] Symmetry operations: (1) $-x, -y, -z$; (2) $x, y, 1 + z$; (3) $-x, -y, 1 - z$.

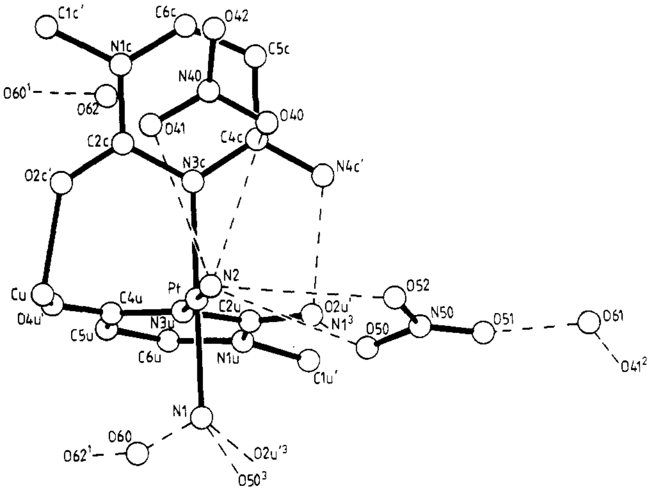

Figure 4. Hydrogen-bonding interactions within the cation (N4c' and O2u'), between the cation and NO_3^- and H_2O, and between H_2O molecules. For distances see Table IV.

All three heavy metals have square-planar coordination spheres, with the Pt being slightly out of the best plane by 0.015 Å in the direction toward the Cu, as in similar compounds.[3a,3c] The coordination planes of Pt and Cu form a 17.8° angle with each other, which is slightly smaller than in a related Pt$_2$,Mn,L$_4$ compound[28] (20.1°; L = 1-MeT = monoanion of 1-methylthymine) and considerably smaller than in dinuclear Pt,M,L$_2$ (M = Pt, Cu) complexes.[3,17] The valence angles around Pt and Cu are close to 90°, and Pt–N and Cu–O distances are normal. The very similar distances between Cu and the coordinating exocyclic oxygens of 1-MeU (1.931 (12) Å) and 1-MeC (1.988 (9) Å) indicate comparable interactions with these sites. This finding is somewhat unexpected since simultaneous metal binding to N3 and O2 of cytosine residues in general leads to short metal–N3 and longer metal–O2 bonds.[8-13] In the dimeric [Ag(1-MeC)NO$_3$]$_2$ complex, which of all examples can best be compared with the heteronuclear Pt$_2$,Cu compound, Ag–N3 is 2.225 (2) Å and Ag–O2 is 2.367 (2) Å.[8]

1-MeU and 1-MeC ligands are planar within the standard deviations as far as the endocyclic atoms are concerned, but O2 of 1-MeU (0.101 Å), O2 of 1-MeC (0.060 Å), Pt (–0.194 Å relative to 1-MeU and 0.235 Å relative to 1-MeC), and Cu (–0.296 Å relative to 1-MeU) are substantially out of the ligand planes (Table III). Deviation of O2 of 1-MeU from coplanarity with the ring probably is a result of its involvement in intramolecular hydrogen bonding with the NH$_2$ (N4) group of 1-MeC (3.00 Å) as well as intermolecular hydrogen-bond formation with NH$_3$ (3.00 Å) (Table IV). Bond lengths and bond angles of the 1-MeC ring do not differ significantly from values observed for free or N3-platinated 1-MeC,[22] and the same is true for the 1-MeU ligand.[3a,29] 1-MeU and 1-MeC rings are roughly perpendicular to the Pt coordination planes as required by the square-planar coordination geometry of Pt and Cu and at a substantial dihedral angle to each other (102.4°).

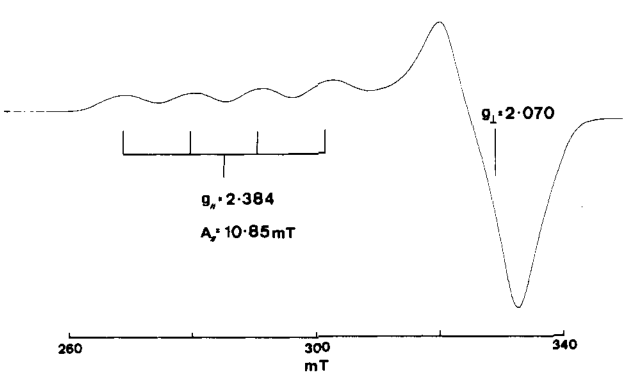

Figure 5. X-Band spectrum of *cis*-[(NH$_3$)$_2$Pt(1-MeU)(1-MeC)Cu-(1-MeC)(1-MeU)Pt(NH$_3$)$_2$]$^{4+}$ (**2**).

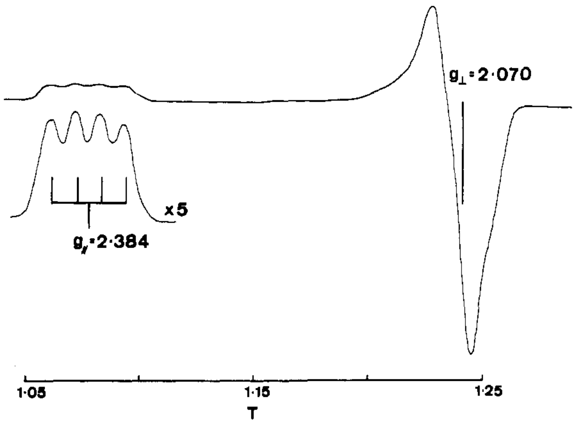

Figure 6. Q-Band spectrum of **2**.

Cations of the title compound are joined by extensive intermolecular hydrogen bonds involving the two NH$_3$ groups of Pt, nitrate oxygens, and water molecules as well as O2 of 1-MeU (Table IV and Figure 4).

EPR Studies. In a previous communication[30] we showed by EPR that the central manganese(II) ion in the trinuclear[28] complex cation *cis*-[(NH$_3$)$_2$Pt(1-MeT)$_2$Mn(1-MeT)$_2$Pt(NH$_3$)$_2$]$^{2+}$ experienced a very large zero-field splitting ($D \gtrsim 1.9$ cm^{-1}, $\lambda = 0.026$). Although the magnitude of D indicates a large axial distortion of the ligand field about the Mn(II) ion, the simplicity of the EPR spectrum prevented determination of the sign of D, and thereby a distinction between axial compression or elongation.

Measurement of the X- and Q-band EPR spectra of the structurally related complex cations *cis*-[(NH$_3$)$_2$Pt(1-MeU)(1-MeC)Cu(1-MeU)(1-MeC)Pt(NH$_3$)$_2$]$^{4+}$ (**2**) and *cis*-[(NH$_3$)$_2$Pt(1-MeU)$_2$Cu(1-MeU)$_2$Pt(NH$_3$)$_2$]$^{2+}$, as the sulfate dodecahydrate (**3**) and the nitrate hexahydrate (**4**), has now enabled us to determine the direction of the tetragonal distortion provided by the axially disposed platinum atoms.

The X-band (~9.5 GHz) spectrum of a polycrystalline sample of **2** is shown in Figure 5. The fact that the $g_\parallel$ absorption (at ~287 mT, split into four components by the copper nuclear hyperfine interaction) is at lower field than the $g_\perp$ band (at ~330 mT) points to a tetragonal elongation of the ligand field about the Cu(II). At Q-band frequency (~

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Table V. Transition Fields (mT) for *cis*-$[(NH_3)_2Pt(1\text{-}MeU)(1\text{-}MeC)Cu(1\text{-}MeC)(1\text{-}MeU)Pt(NH_3)_2]^{4+}$ (**2**) ($g_\parallel = 2.384, g_\perp = 2.070, A_\parallel = 10.85$ mT)

X-band (9.514 GHz)		Q-band (35.98 GHz)	
calcd	obsd	calcd	obsd
268.8	269.2	1062.2	1059.9
279.7	280.1	1072.0	1070.7
290.5	291.3	1083.7	1081.6
301.4	302.5	1094.6	1091.7
328.4	329.3	1241.9	1239.1

Table VI. Transition Fields (mT) for *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Cu(1\text{-}MeU)_2Pt(NH_3)_2]^{2+}$

(a) Sulfate (**3**) ($g_\parallel = 2.367, g_\perp = 2.058, A_\parallel = 12.14$ mT)

X-band (9.511 GHz)		Q-band (35.982 GHz)	
calcd	obsd	calcd	obsd
268.9	268.6	1067.9	1068.6
281.0	280.6	1080.1	1080.9
293.2	292.6	1092.2	1093.2
305.3	304.6	1104.3	1105.4
330.3	330.2	1249.2	1249.2

(b) Nitrate (**4**) ($g_\parallel = 2.362, g_\perp = 2.056, A_\parallel = 12.38$ mT)

X-band (9.514 GHz)		Q-band (35.984 GHz)	
calcd	obsd	calcd	obsd
269.2	269.8	1069.9	1069.2
281.6	281.9	1082.3	1081.8
294.0	293.9	1094.7	1094.7
306.4	306.3	1107.1	1107.0
330.6	331.3	1250.5	1249.7

35.98 GHz) the spectrum is better resolved (Figure 6) with $g_\parallel$ at ~1085 mT and $g_\perp$ at ~1250 mT. A correlation between the observed transition fields and those calculated from the parameters $g_\parallel = 2.384$, $g_\perp = 2.070$, and $A_\parallel = 10.85$ mT is given in Table V.

The small rhombic component to the tetragonal field about the copper(II) ions shown by the X-ray study [Cu–Oc = 1.988 Å; Cu–Ou = 1.931 Å] is not clearly resolved in the $g_\perp$ absorption, though the band shows asymmetry.

The EPR spectra of **3** and **4** are very similar to those of **2**, supporting the suggestion made previously[3a] that they also have a trinuclear structure of the type reported here for **2**. As expected, the parameters derived for **3** and **4** (Table VI) show little anion dependence. However, replacing two of the four 1-MeU ligands in **3** and **4** by two 1-MeC ligands, as in **2**, causes an increase in $g_\parallel$ and $g_\perp$ and a reduction in $A_\parallel$ (from ~12.25 to 10.85 mT). Without X-ray structural information on **3** and **4** one cannot accurately correlate such differences in $A_\parallel$ with changes in the Cu–O bond lengths for the two types of ligand system. A much more striking difference is observed in the EPR spectra of the dinuclear cation *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Cu(H_2O)_2]^{2+}$ (**5**). It was previously shown[3a] that, in the sulfate salt, two such cations pack in a centrosymmetric head–head arrangement. At that time[3a] the separation (3.483 Å) between the copper atoms in these cation pairs was regarded as being too long for there to be any significant Cu–Cu interaction. Subsequent X-band EPR measurements (Figure 7) have shown that this conclusion was not correct.

Spectra such as that shown in Figure 7 are typical of those given by dipolar coupled pairs of Cu(II) ions.[31] A particularly characteristic feature is the presence of the multicomponent $\Delta m = 2$ absorption at ~140 mT (Figure 8). The $\Delta m = 1$ region, at higher field, at X-band frequency has the *z* components overlapping the *x* and *y* absorptions. Better resolution in this region is achieved at Q-band (Figure 9), and two *z* components (apparently unsplit by Cu nuclear hyperfine coupling) are seen at 1049 and 1108 mT. The complexity of the spectrum in the $\Delta m = 1$ *x* and *y* region (1.2–1.3 T at Q-band) is consistent with the rhombic symmetry found in the X-ray study.[3a]

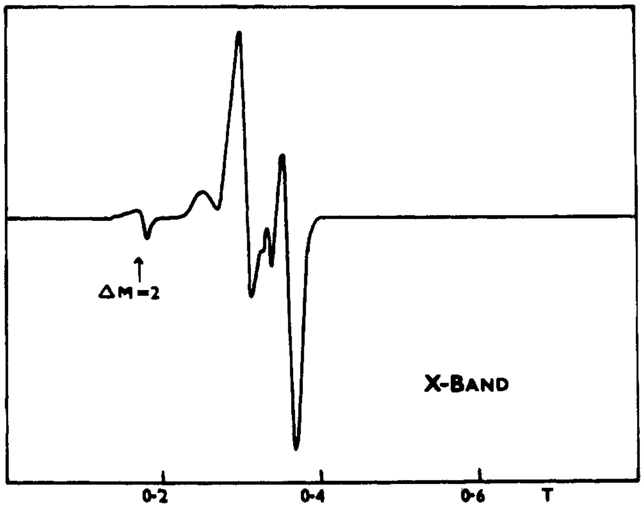

Figure 7. X-Band spectrum of *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Cu(H_2O)_2]^{2+}$ (**5**).

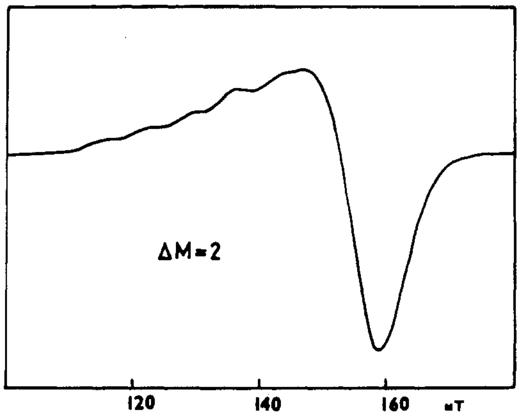

Figure 8. X-Band spectrum of **5**, $\Delta m = 2$ transition.

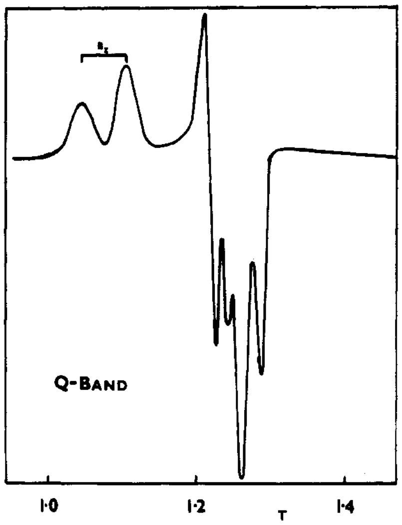

Figure 9. Q-Band spectrum of **5**.

One interesting observation from the Q-band spectrum is that no $\Delta m = 2$ absorption was found at that frequency even at very high instrument gain. A diminution in the intensity of this "forbidden" signal would be expected as one increases the microwave energy, and this effect is clearly demonstrated

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in the spectra obtained for this compound. Virtually all previous studies on coupled Cu(II) systems have employed only X-band measurements. We have observed[32] a similar diminution in the intensity of the $\Delta m = 2$ absorption on changing from X- to Q-band for the dimeric[33] complex $[Cu(adenine)_2(H_2O)]_2 \cdot 6H_2O$, though for that compound, in which the coupling is much stronger,[34] the $\Delta m = 2$ band can still be seen very weakly at Q-band with very high spectrometer gain settings. These observations emphasize the value of changing the applied microwave frequency in studying coupled copper(II) systems.

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Registry No. **1**, 91003-29-1; **2**, 91032-24-5; **3**, 83351-00-2; **4**, 83434-36-0; **5**, 83378-74-9; 1-MeUH, 615-77-0; *cis*-$(NH_3)_2Pt$(1-MeU)Cl, 85715-78-2.

Supplementary Material Available: Listings of atomic parameters, observed and calculated structure factors, and least-squares planes (Pt and Cu coordination planes, 1-MeU and 1-MeC planes) (13 pages). Ordering information is given on any current masthead page.

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Copper(I) Complexes with Unsaturated Small Molecules. Preparation and Structural Characterization of Copper(I)–Di-2-pyridylamine Complexes with Olefins, Acetylene, and Carbon Monoxide

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The syntheses, spectroscopy, and structures of Cu(I)–di-2-pyridylamine ($NH(py)_2$) complexes with ethylene, propylene, acetylene, and carbon monoxide ligands are presented. Complexes of the formulation $[Cu(NH(py)_2)(X)]Y$ ($X = C_2H_4$ and C_3H_6, $Y = ClO_4$; $X = C_2H_2$, $Y = BF_4$) and $[Cu(NH(py)_2)(CO)ClO_4]$ are characterized analytically and spectroscopically. The ethylene, acetylene, and carbonyl compounds are also characterized by X-ray diffraction techniques. The ethylene complex $[Cu(NH(py)_2)(C_2H_4)]ClO_4$ crystallizes in the monoclinic space group $C2/c$ with 4 molecules per unit cell of dimensions $a = 9.829$ (1) Å, $b = 17.105$ (2) Å, $c = 8.672$ (1) Å, and $\beta = 93.806$ (1)° at −100 °C. Least-squares refinement of 116 variables led to a value of the conventional R index (on F) of 0.050 and of R_w of 0.049 for 1260 reflections having $F_o^2 > 2\sigma(F_o^2)$. The geometry about the Cu(I) ion, which is coordinated to two pyridyl nitrogen atoms and an ethylene molecule, is trigonal planar. The carbon–carbon bond distance of the coordinated ethylene molecule is 1.359 (7) Å. The acetylene complex $[Cu(NH(py)_2)(C_2H_2)]BF_4$ crystallizes in the monoclinic space group $C2/c$ with 4 molecules per unit cell of dimensions $a = 10.140$ (2) Å, $b = 17.782$ (4) Å, $c = 7.852$ (1) Å, and $\beta = 105.34$ (1)° at −100 °C. Least-squares refinement of 119 variables led to a value of the conventional R index of 0.046 and of R_w of 0.044 for 1259 independent reflections having $F_o^2 > 2\sigma(F_o^2)$. The coordination sphere about the Cu(I) ion is analogous to that found for the ethylene complex. The carbon–carbon bond distance of the coordinated acetylene molecule is 1.188 (11) Å. The carbonyl complex $[Cu(NH(py)_2)(CO)ClO_4]$ crystallizes in the triclinic space group $P\bar{1}$ with 2 molecules per unit cell of dimensions $a = 8.922$ (1) Å, $b = 10.755$ (1) Å, $c = 7.379$ (1) Å, $\alpha = 91.51$ (1)°, $\beta = 99.24$ (1)°, and $\gamma = 81.25$ (1)° at −100 °C. Least-squares refinement of 226 variables led to a value of the conventional R index of 0.028 and of R_w of 0.032 for 2774 independent reflections having $F_o^2 > 2\sigma(F_o^2)$. The Cu(I) ion is coordinated to two pyridyl nitrogen atoms and a carbonyl group in a trigonal-planar geometry. There is also a perchlorate oxygen atom at a distance of 2.429 (1) Å from the copper ion, which suggests a weak interaction between cation and anion. These complexes demonstrate that the copper coordination chemistry with ethylene, propylene, acetylene, and carbon monoxide is consistent with the proposed role of copper at the ethylene binding site of plants.

Recently we reported the synthesis, properties, and first structural characterization of two Cu(I)–ethylene complexes that are stable to loss of olefin, unlike the majority of previously reported cuprous–ethylene adducts.[1] Our interest in this area arises from the proposed role of copper in the binding of the plant hormone ethylene to its receptor site.[2,3] Although the identity of the binding site remains unknown, the properties of the native systems suggest the involvement of a metal ion. Of all the biologically important transition metals, only copper ion shows reactivity with ethylene and the ethylene analogues (propylene, acetylene, carbon monoxide) in an oxidation state commonly found in biological systems. However, the majority of Cu(I)–ethylene adducts are so unstable to loss of olefin that they have been in general only poorly characterized.[4-6] In contrast, the native systems show an apparent K_D for ethylene of $\sim 10^{-10}$ M.[7] It is thus impossible to determine whether or

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