The Crystal Structure of a Heteronuclear Pt_2CuL_4 Complex of 1-Methyluracil, $Cu[Pt(NH_3)_2(C_5H_5N_2O_2)_2]_2SO_4\cdot 8H_2O$

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Abstract

The crystal structure of heteronuclear bis[bis(μ-1-methyluracilato-*N*3,*O*4)-*cis*-diammineplatinum(II)]-copper(II) sulfate octahydrate, $Cu[Pt(NH_3)_2(C_5H_5N_2O_2)_2]_2SO_4\cdot 8H_2O$, has been determined by X-ray diffraction. The compound crystallizes in space group $I4_1/a$ with cell parameters $a = 20.470(7)$, $c = 23.509(8)$ Å, $V = 9850(6)$ Å^3, $Z = 8$. The structure was refined on 2783 reflections to $R = 0.045$ and $R_w = 0.064$. The deprotonated 1-methyluracilato ligand coordinates to *cis*-$Pt(NH_3)_2^{2+}$ by N3 and to Cu by O4. Both the Pt and Cu have square-planar coordination spheres with Cu in the inversion center of the trinuclear Pt_2Cu unit. The Pt–Cu distances within the cation are 2.684(1) Å. The non-coordinating O2 oxygens take part in a hydrogen bond network with NH_3 groups of the adjacent molecular cations.

Introduction

Platinum(II) binding to N3 of the neutral uracil or its derivatives leads to a delocalization of the electron lone pair at N3 into the ring. This increases the basicity of the exocyclic oxygens O4 and O2 and thus promotes the binding of other metal ions to them [1–3]. There is good evidence that of these oxygens O4 is the best nucleophilic site, while O2 is a weaker ligand [4–6]. As part of a systematic investigation of the ligating properties of the pyrimidine nucleobases 1-methylcytosine (1-MeC), 1-methylthymine (1-MeT) and 1-methyluracil (1-MeU), we have recently prepared a series of mixed metal Pt_2M trimeric complexes where M = Cu(II), Ni(II), Co(II), Fe(II) or Mn(II) [7–11].

Single crystal X-ray studies have revealed the Mn-centered and Cu-centered complexes as being trimeric structures with quite similar geometries. In both complexes the central metal is situated on a crystallographic inversion center, resulting in a coplanar $M(O4)_4$-arrangement. The terminal Pt(II) ions complete the distorted octahedral coordination sphere about the central metal at Pt–M distances of about 2.70 Å. According to spectral studies, it seems very likely that a similar geometry occurs for the other molecules in the series [11]. Because of the relatively short Pt–M distances the question concerning the nature of the interaction between the Pt(II) ions and the central metal is of particular interest. The 'd–d' transition energies and EPR parameters of the Cu(II) ion suggest that the Pt(II) ions effectively function as ligands which, despite their formal positive charge, produce a weak s-antibonding perturbation on the copper(II) $3d_{z^2}$-orbitals [12]. As a part of our studies of the structural characterization of mixed metal (Pt_2M)-trimers we have determined the structure of bis[bis(μ-1-methyluracilato)-*cis*-diammineplatinum(II)]copper(II) sulfate octahydrate by X-ray crystallography.

Experimental

The Pt_2Cu compound was prepared by mixing 1 mmol of *cis*-$(NH_3)_2Pt(1\text{-}MeU)_2\cdot 4H_2O$ [8] and 0.25 mmol of $CuSO_4\cdot 5H_2O$ in 10 ml of water, and allowing the yellow–green solution to evaporate. Besides unreacted Pt starting compound (140 mg), a total of 260 mg of green octahedrons of the Pt_2Cu complex were harvested in several fractions (yield 38%). Crystals of the various fractions always lost water of crystallization when kept in air. However, differences in behavior were observed in that loss of water was accompanied by: rapid and complete loss of transparency (crystals completely opaque); partial transparency loss (crystal surface still shiny, internal fracturing); or no apparent change at all (crystals stay transparent, even after 2 years of storage). Elemental analysis data strongly depended on the

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time of storage. Immediately after isolation, data were consistent with approximately 13.5 H_2O per Pt_2Cu unit. *Anal.* Calc. for $[Pt_2(NH_3)_4(C_5H_5N_2O_2)_4Cu]SO_4\cdot 13.5H_2O$: C, 17.64; H, 4.38; O, 29.96; Cu, 4.67. Found: C, 17.23; H, 4.52; O, 29.54; Cu, 4.4%. Other samples, analysed slightly later, showed the presence of 12 H_2O [8] or 11 H_2O (e.g., Calc.: C, 18.24; H, 4.14; O, 27.95; Cu, 4.83. Found: C, 18.22; H, 4.13; O, 27.96; Cu, 4.74%). After 2 years of storage, a sample which originally analysed as a 13.5-hydrate and had stayed transparent during this time, indicated the presence of only 7–8 water molecules per Pt_2Cu (Calc. for 7.5 H_2O: C, 19.16; H, 3.79; N, 13.41. Found: C, 18.80; H, 3.93; N, 13.32%). These data are in agreement with thermogravimetric measurements (Netzsch 429) of two aged samples (transparent crystals and partially transparent ones) which indicated a 10.4–11.3% loss of weight between 40 °C and 125 °C (no further loss before decomposition above 260 °C), consistent with 7.2–7.9 H_2O.

Density measurements on a series of different crystals (in CH_3I/CCL_4) gave 1.95 g cm^{-3} for samples immediately after isolation and somewhat variable values (1.90 to 1.85) for aged samples. Since we did not measure a density as low as expected from the X-ray work (1.70), we are not certain as to whether the crystal selected for X-ray work was identical with the bulk material or a minor component only. Attempts to solve this question by determining the cell constants of other crystals were unsuccessful due to their poor qualities.

A crystal of dimensions 0.45 X 0.4 X 0.4 mm was sealed in a capillary tube and used for X-ray measurements. Crystal data were measured at room temperature (291 K) on a Nicolet P3F single-crystal diffractometer using graphite monochromatized Mo Kα radiation (λ = 0.71069 Å). The cell parameters were determined by least-squares treatment of the adjusted angular settings of 25 reflections ($9° < 2\theta < 24.5°$). The crystal data are $a = 20.470(7)$, $c = 23.509$ Å, $V = 9850(6)$ Å^3, space group $I4_1/a$ (No. 88), D_{calc} 1.70 g cm^{-3}, $Z = 8$, formula weight = 1334.9 and $F(000) = 4552$. The space group was confirmed by systematic absences *hkl* with $h + k + l$ odd, *hk*0 with $h + k$ odd and 00*l* with *l* odd. The intensity data were collected by an $\omega - 2\theta$ scan technique at variable scan rates of 1.5 to 29.3 °min^{-1} depending on the number of counts measured in a fast preliminary scan. Up to a maximum value of $2\theta = 50°$, h 0→25, k 0→25 and l 0→28, 4783 reflections were measured, resulting in a set of 3458 unique reflections. Of these, 2783 were considered as observed ($I_o > 3\sigma(I_o)$). Standard reflections (480, 251, 134, 268) measured every 50 reflections showed the intensity variation was random and within 1% with respect to the mean. The intensities were corrected for Lorentz and polarization effects but corrections for extinction were considered unnecessary.

An empirical absorption correction ($\mu = 65.2$ cm^{-1}) was made by ϕ-scan of five reflections. The range of the correction factors applied to the intensities was 0.729 to 1.000.

The structure was solved by the Patterson method. Successive Fourier calculations and full-matrix least-squares refinement with non-hydrogen atoms anisotropic, waters of crystallization as isotropic and fixed, and hydrogen atoms with $U = 0.05$ Å^2 and fixed, led to $R = 0.045$ and $R_w = 0.064$ ($R_w = [\Sigma w(|F_o| - |F_c|)^2/w|F_o|]^{1/2}$, with $w = 1/\sigma(|F_o|)^2$). After the last cycle $\Delta/\sigma_{av} = 0.0004$ and $\Delta/\sigma_{max} = 0.005$. The oxygen atoms of the sulfate ion did not show up in the final difference map. The probable reason for this is that the population parameter of the sulfate group is 0.5 and the group is rotationally disordered. Six of the eight molecules of water of crystallization could be unambiguously found. The rest of the water molecules were probably disordered because in the vicinity of the defined water molecules the final difference map revealed several rather small peaks, probably caused by the undefined water molecules. The maximum peak in the final difference map was 0.99 e Å^{-3} and this was situated in the vicinity of Pt. Scattering factors were from Cromer and Mann [13] and the anomalous dispersion corrections were applied [14]. All calculations were carried out on a UNIVAC 1100/61 E computer with X-RAY 76 [15] and a program MPLN for planes [16].

Results and Discussion

An ORTEP [17] drawing of the cation of bis-[bis(μ-1-methyluracilato)-*cis*-diammineplatinum(II)]-copper(II) sulfate octahydrate is shown in Fig. 1 and the packing of the cations in Fig. 2. The atomic parameters are listed in Table I, selected interatomic distances and angles in Table II, dihedral angles (°) between various planes in Table III and intermolecular distances in Table IV.

Each platinum is coordinated by two NH_3 molecules *cis* to each other and by two N3 atoms of the 1-MeU ligands, thus leading to the square-planar coordination about the Pt(II) ion. As with other compounds of the same type [1, 6, 9], the molecular cation is centrosymmetric with the copper situated in the inversion center. Because of the space group symmetry, the copper(II) ion has a square-planar coordination sphere with the exocyclic oxygen atoms of the uracilato ligands as donor atoms. Contrary to 1-MeT, there exists no pseudo two-fold axis through N3 and C6 in 1-MeU, and thus O4 and O41 exocyclic oxygens can unambiguously be assigned as the donor atoms. This agrees well with the prediction that O4 is the most nucleophilic site once N3 is bound to a metal. Thus each nucleobase acts as a bidentate ligand. The Pt–Cu distance within the trinuclear

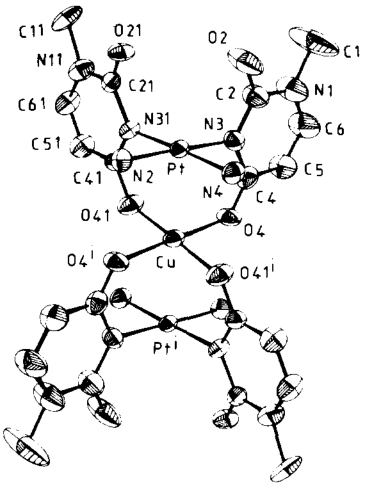

Fig. 1. An ORTEP drawing and the numbering scheme of the molecular cation of bis[bis(μ-1-methyluracilato)*cis*-diammineplatinum(II)]copper(II) sulfate octahydrate. The hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

cation is 2.684(1) Å, which is comparable to the related trinuclear complexes containing two Pt(II) ions and a Mn(II) ion (2.704(1) Å [7]) or Cu(II) ion (2.681(1) Å [9]). The rather short intermetallic distance within the complex cation does not indicate strong interaction between Pt and Cu, but is mainly a consequence of the bite distance of N3 and O4 in the 1-MeU ligand and of the coordination geometries of Pt(II) and Cu(II) ions.

All three metal ions have square-planar coordination spheres with the Pt being slightly out of the best plane by 0.027(1) Å, pointing away from the Cu. This is in contrast to related compounds [6, 9] in which the Pt atoms are oriented slightly towards the center metal ion. The spectroscopic results [11, 12] indicate that the Pt(II) ions in these complexes are functioning as weak σ-donors via the filled $5d_{z^2}$-orbitals interacting with the Cu(II) $3d_{z^2}$-orbital. The Pt(II) ion can thus be considered as a ligand, despite its formal positive charge.

The coordination planes of Pt and Cu form an angle of 15.7° with each other. This is slightly smaller than in related compounds (17.8° and 20.1°) [6, 9] and may be the reason for the Pt atoms moving away from the Cu. The Pt and Cu coordination planes are twisted about the Pt–Cu axis by an average of 3.7°, which is less than in the Pt_2MnL_4 complex (10.9°) [6] and about the same as in the Pt_2CuL_4 complex (2.8°) [9]. The Pt–N and Cu–O distances are normal and the angles in the Pt and Cu coordination spheres are close to 90°. The 1-MeU ligands are planar within the standard deviations and the dihedral angle between the rings is 89.2(7)°. The dihedral angles between the Pt coordination plane and the 1-MeU rings are 92.1(5)° and 79.9(4)°.

The cations of the title compound are joined together by an extensive intermolecular hydrogen bond network which involves the two NH_3 groups, exocyclic O2 and O21 oxygens, sulfate anion and the water of crystallization. The sulfate anion forms a short contact with the N4 of the ammonia group, so that the S1–N4 distance is 2.93(3) Å. Because of the space group symmetry only half of the sulfate group could be determined and the group was probably rotationally disordered so that no sulfate oxygens could be determined and no detailed picture of this contact system could be obtained. According to elemental analysis, the aged crystals contain between seven and eight water molecules per Pt_2Cu unit, but only six of them could unambiguously be localized in the structure determination. The localized water molecules filled, along with some residual electron density, a cavity between the molecular cations and formed a hydrogen bond network with each other and with the sulfate anion. The details of the hydrogen bond network are given in Table III.

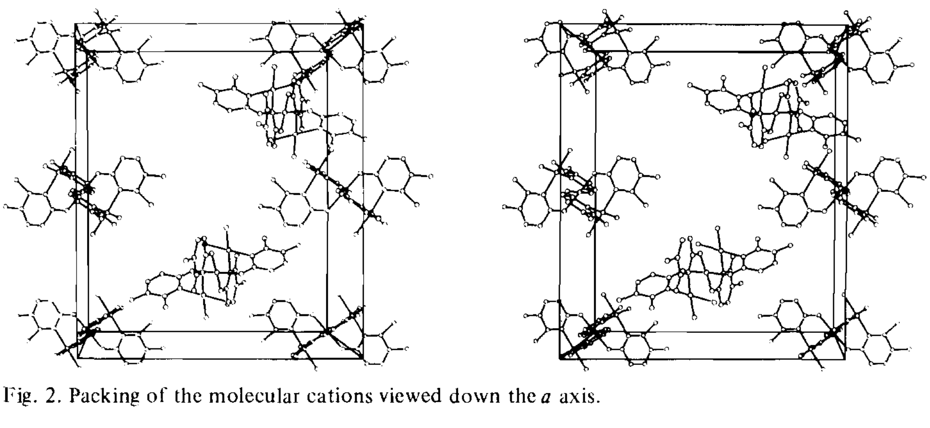

Fig. 2. Packing of the molecular cations viewed down the *a* axis.

TABLE I. Fractional Atomic Coordinates ($\times 10^4$) and U_{eq} ($\times 10^3$ Å^2)[a] with Standard Deviations in Parentheses[b]

Atom	*x*	*y*	*z*	U_{eq} (Å^2)
Pt	498(.3)	952(.3)	655(.3)	34(.4)
Cu	0	0	0	42(2)
S1	3087(11)	3873(12)	861(11)	192(22)
N2	−374(6)	1394(6)	838(6)	41(8)
N4	393(7)	415(7)	1383(6)	46(9)
N3	1344(7)	494(7)	479(6)	48(9)
C4	1373(10)	−74(9)	157(8)	49(11)
O4	881(6)	−333(6)	−32(6)	54(8)
C5	1988(10)	−344(10)	71(11)	71(15)
C6	2514(11)	−78(13)	299(13)	94(20)
N1	2494(8)	482(9)	621(10)	91(15)
C1	3085(13)	823(19)	815(22)	245(44)
C2	1886(10)	778(10)	705(11)	70(14)
O2	1866(7)	1276(9)	1014(9)	115(15)
N31	578(7)	1463(6)	−76(6)	38(8)
C41	430(8)	1190(8)	−584(8)	44(11)
O41	203(7)	609(5)	−609(5)	58(8)
C51	502(10)	1563(10)	−1099(8)	56(13)
C61	739(10)	2156(10)	−1070(8)	58(13)
N11	897(7)	2428(7)	−551(7)	56(11)
C11	1193(12)	3101(9)	−492(10)	77(15)
C21	799(7)	2102(8)	−34(8)	40(10)
O21	897(6)	2373(5)	412(5)	51(8)
O5	4240	112	2138	134
O6	3667	5220	1014	238
O7	4806	144	944	179
H1	−590	1714	635	50
H2	−388	1480	1206	50
H3	−721	1087	714	50
H4	773	80	1421	50
H5	387	709	1736	50
H6	−14	197	1324	50
H7	2049	−698	−138	50
H8	2828	0	143	50
H9	3102	1254	867	50
H10	3516	545	714	50
H11	3088	663	1334	50
H12	347	1319	−1537	50
H13	787	2392	−1500	50
H14	1049	3406	−645	50
H15	1229	3202	−46	50
H16	1697	3050	−678	50

[a] $U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} \bar{a}^*_i \bar{a}^*_j \bar{a}_i \bar{a}_j$ [18]. [b] For O5, O6, O7 and hydrogen atoms the isotropic temperature factors are given.

Supplementary Material

Equations for planes in Table III are available from the authors on request.

Acknowledgement

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TABLE II. Interatomic Distances (Å) and Angles (°) with e.s.d.s in Parentheses

Pt–Cu	2.685(1)	Pt–N2	2.047(12)
Pt–N4	2.045(14)	Pt–N3	2.012(14)
Pt–N31	2.019(14)	Cu–O4	1.929(12)
Cu–O41	1.943(11)	N1–C1	1.469(37)
N1–C2	1.398(27)	C2–O2	1.252(30)
C2–N3	1.361(26)	N3–C4	1.389(23)
C4–O4	1.222(24)	C4–C5	1.390(29)
C5–C6	1.320(33)	C6–N1	1.374(34)
N11–C11	1.511(24)	N11–C21	1.401(24)
C21–O21	1.203(22)	C21–N31	1.388(21)
N31–C41	1.353(23)	C41–O41	1.278(20)
C41–C51	1.439(27)	C51–C61	1.309(29)
C61–N11	1.380(25)	N3–O4	2.282(19)
N31–O41	2.284(17)		
N2–Pt–N4	98.3(6)	N2–Pt–N3	178.5(5)
N2–Pt–N31	91.2(6)	N4–Pt–N3	90.7(6)
N4–Pt–N31	178.1(6)	N3–Pt–N31	89.8(6)
O4–Cu–O41	89.9(6)	C6–N1–C2	122(2)
N1–C2–N3	119(2)	C2–N3–C4	122(2)
N3–C4–C5	117(2)	C4–C5–C6	121(2)
C5–C6–N1	123(2)	Pt–N3–C4	123(1)
N3–C4–O4	122(1)	C4–O4–Cu	127(1)
C61–N11–C21	114(2)	N11–C21–N31	116(2)
C21–N31–C41	122(1)	N31–C41–C51	120(2)
C41–C51–C61	119(2)	C51–C61–N11	120(2)
Pt–N31–C41	121(1)	N31–C41–O41	120(2)
C41–O41–Cu	130(1)		

TABLE III. Dihedral Angles (°) between Various Planes[a]

Pt coord. plane/1-MeU plane	92.1(5)	Pt coord. plane/1-MeU′ plane	79.9(4)
1-MeU plane/1-MeU′ plane	89.2(7)	Cu coord. plane/1-MeU plane	81.3(5)
Cu coord. plane/1-MeU′ plane	91.2(5)	Cu coord. plane/Pt coord. plane	15.7(1.1)

[a] Equations are given in Supplementary Material.

TABLE IV. Possible Hydrogen Bond Interactions (Å)

S1–O6[a]	3.02(2)	O5–O7[a]	3.04
O21–N2[b]	2.92(2)	N2–O2[c]	2.79(2)
N2–O21[c]	3.01(2)	N4–S1[c]	2.93(3)
N4–O21[c]	3.13(2)		

[a] x, y, z. [b] $-x, -y + \frac{1}{2}, z$. [c] $y - \frac{1}{4}, -x + \frac{1}{4}, -z + \frac{1}{4}$.

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