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Transition-Metal–Nucleoside Complexes. The Crystal and Molecular Structure of (Glycylglycinato)(cytidine)copper(II) Dihydrate

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Details of the molecular and crystal structure of the nucleoside complex (glycylglycinato)(cytidine)copper(II) are reported. The complex crystallizes in the monoclinic system, space group $P2_1$, with crystal data: $a = 4.710(4)$, $b = 26.99(3)$, $c = 14.99(2)$ Å, $\beta = 90.1(1)^\circ$; $D_m = 1.67(2)$, $D_c = 1.64$ g cm $^{-3}$. There are two independent, but closely related, complexes and four waters of crystallization per asymmetric volume. Intensities for 2190 symmetry-independent reflections were collected by counter methods with the θ – 2θ scan technique and graphite-monochromatized Mo $K\alpha$ radiation. The structure was solved by standard heavy-atom Patterson and Fourier methods. Full-matrix least-squares refinement, based on F , led to final R values of 0.144 (all data) and 0.127 [the 1852 reflections with $F_o \geq 3\sigma(F_o)$]. The coordination geometry about the Cu is pseudo-square pyramidal with the tridentate glycylglycinato dianion and N(3) of the cytidine ligand occupying the equatorial plane, and O(2) of cytidine approximately in an axial position. The cytidine ligand is thus chelated to the Cu^{II} center employing an equatorial position *via* N(3) and an axial position *via* O(2). The two complexes in the asymmetric unit have nearly identical molecular conformations and are related by a local twofold axis parallel to **a**. The conformation of the cytidine ligand is very similar to that found in uncomplexed cytidine. The complete crystal structure is maintained by an extensive hydrogen-bonding network and columnar stacking of the complexes along **a**.

Introduction

Solution (Marzilli, 1977) and crystallographic (Hodgson, 1977) studies on the binding of metal ions and metal complexes to nucleic acids and nucleic acid constituents have recently been comprehensively reviewed. The crystallographic work (Hodgson, 1977) has centered on the binding of metal species to purines, pyrimidines, alkylated purines and pyrimidines, nucleosides and nucleotides. Of these ligand types, the nucleosides have been the least studied by crystallographic techniques, primarily because of synthetic difficulties, very low stability constants, and the low solubility of the nucleosides themselves.

In fact we know of only four crystallographic studies on metal–nucleoside complexes: (1) the bispyridine osmate ester of adenosine (Conn, Kim, Suddath, Blattmann & Rich, 1974); (2) the present cytidine complex (Szalda, Marzilli & Kistenmacher, 1975a); (3) the [(ethylenediamine)bis(guanosine)platinum(II)]²⁺ complex cation (Gellert & Bau, 1975); (4) the deoxyadenosine complex of bis(acetylacetonato)nitrocobalt(III) (Sorrell, Epps, Kistenmacher & Marzilli, 1977).

Perhaps the most interesting feature which has emerged from the crystallographic studies on metal–nucleoside complexes is the chelation of cytidine *via* N(3) and O(2) to Cu^{II} (Szalda, Marzilli & Kistenmacher, 1975a). Verification of the importance of such

chelation has been derived from the study of three N(3),O(2)-bonded copper(II)-cytosine complexes [dichlorobis(cytosine)copper(II) (Sundaralingam & Carrabine, 1971); (glycylglycinato)(cytosine)copper(II) (Kistenmacher, Szalda & Marzilli, 1975; Saito, Terashima, Sakaki & Tomita, 1974); and (*N*-salicylidine-*N'*-methylethylenediamine)(cytosine)copper(II) (Szalda, Marzilli & Kistenmacher, 1975*b*)].

The preparation of the cytidine complex of glycylglycinatocopper(II) has been described (Szalda, Marzilli & Kistenmacher, 1975*a*). Prismatic needles were obtained by slowly diffusing methanol into an aqueous solution of the complex. The 'best' crystals were (in general) small, fragile, poor scatterers and very difficult to produce. Preliminary oscillation and Weissenberg photographs showed nearly orthorhombic symmetry (*mmm*), but a careful diffractometer study showed that the true diffraction symmetry was only *2/m* and, therefore, that the lattice was monoclinic. The

only observed systematic absences were $0k0, k = 2n + 1$, consistent with the space group $P2_1$. The measured density of $1.67(2) \text{ g cm}^{-3}$ indicated two complexes plus four lattice waters per asymmetric volume. In fact (see below), the two independent complexes are related by a local twofold axis along **a**, which is responsible for the nearly orthorhombic symmetry of the intensity-weighted reciprocal lattice.

The intensity data were obtained from a prismatic needle with faces (100), ($\bar{1}00$), (001), ($00\bar{1}$), (010) and ($0\bar{1}0$). The separation between opposite pairs of faces is as follows: (100) and ($\bar{1}00$), 0.035 cm; (001) and ($00\bar{1}$), 0.015 cm; (010) and ($0\bar{1}0$), 0.008 cm. The crystal was mounted approximately along **a** for data collection.

The 2734 reflections in the *hkl* and *hk\bar{l}* octants to $2\theta = 45^\circ$ were measured on a Syntex $P\bar{1}$, computer-controlled diffractometer, with graphite-monochromatized $\text{Mo } K\bar{\alpha}$ radiation. Intensity data were collected in the $\theta-2\theta$ scan mode; individual scan speeds were deter-

Table 1. Final atomic parameters

The Cu atom parameters are $\times 10^4$. All other atom positional parameters are $\times 10^3$. Estimated standard deviations in the least significant figure are enclosed in parentheses. The form of the anisotropic ellipsoid for the Cu atoms is:

$$\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)].$$

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> ₁₁ | <i>B</i> ₂₂ | <i>B</i> ₃₃ | <i>B</i> ₁₂ | <i>B</i> ₁₃ | <i>B</i> ₂₃ |
|-------|----------|----------|----------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Cu(1) | 1086 (7) | 0 | 378 (2) | 387 (18) | 14 (1) | 29 (2) | -5 (3) | -9 (4) | 4 (1) |
| Cu(2) | 742 (7) | 1538 (2) | 4139 (2) | 415 (19) | 11 (1) | 34 (2) | 2 (3) | 14 (4) | 2 (1) |
| | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> | |
| O(2) | 402 (4) | 54 (1) | -92 (1) | 3.6 (4) | O(22) | 382 (4) | 109 (1) | 544 (1) | 4.5 (4) |
| O(7) | 388 (4) | 5 (1) | 139 (1) | 3.8 (4) | O(27) | 382 (4) | 148 (1) | 320 (1) | 3.7 (4) |
| O(8) | 557 (5) | -40 (1) | 257 (1) | 5.3 (5) | O(28) | 561 (4) | 185 (1) | 205 (1) | 3.9 (5) |
| O(9) | -107 (5) | -143 (1) | 55 (1) | 6.9 (6) | O(29) | -118 (4) | 297 (1) | 388 (1) | 2.7 (4) |
| O(1') | 671 (4) | 195 (1) | -127 (1) | 3.4 (4) | O(21') | 681 (4) | -34 (1) | 578 (1) | 3.8 (4) |
| O(2') | 606 (4) | 137 (1) | -300 (1) | 4.6 (5) | O(22') | 634 (4) | 23 (1) | 744 (1) | 4.8 (5) |
| O(3') | 244 (4) | 218 (1) | -330 (1) | 4.8 (5) | O(23') | 291 (4) | -62 (1) | 777 (1) | 4.3 (5) |
| O(5') | 388 (6) | 278 (1) | -82 (2) | 8.1 (7) | O(25') | 387 (4) | -124 (1) | 543 (1) | 3.4 (4) |
| O(41) | 877 (5) | 345 (1) | 222 (1) | 5.7 (5) | N(21) | 337 (5) | 23 (1) | 521 (2) | 4.7 (6) |
| O(42) | 39 (6) | 313 (1) | 662 (2) | 8.6 (8) | N(23) | 75 (4) | 80 (1) | 436 (1) | 2.8 (4) |
| O(43) | 508 (6) | 373 (1) | 642 (2) | 7.1 (7) | N(24) | -281 (5) | 56 (1) | 334 (1) | 3.5 (5) |
| O(44) | 653 (9) | 275 (2) | 89 (3) | 13.7 (1.2) | N(28) | 79 (5) | 216 (1) | 374 (2) | 4.0 (5) |
| N(1) | 348 (4) | 134 (1) | -65 (1) | 2.6 (4) | N(30) | -129 (5) | 185 (1) | 518 (1) | 4.5 (5) |
| N(3) | 110 (4) | 73 (1) | 18 (1) | 1.6 (4) | C(22) | 279 (5) | 72 (1) | 501 (2) | 2.6 (5) |
| N(4) | -241 (5) | 98 (1) | 122 (2) | 5.2 (6) | C(24) | -64 (6) | 47 (1) | 393 (2) | 2.7 (6) |
| N(8) | 92 (5) | -71 (1) | 72 (4) | 2.8 (5) | C(25) | 31 (5) | -5 (1) | 403 (2) | 3.2 (6) |
| N(10) | -132 (5) | -24 (1) | -71 (2) | 4.5 (6) | C(26) | 216 (6) | -12 (1) | 467 (2) | 4.4 (6) |
| C(2) | 297 (5) | 87 (1) | -46 (2) | 1.9 (5) | C(27) | 422 (6) | 184 (1) | 273 (2) | 3.5 (6) |
| C(4) | -43 (5) | 110 (1) | 68 (2) | 2.7 (5) | C(28) | 238 (6) | 231 (1) | 288 (2) | 3.4 (6) |
| C(5) | 37 (6) | 161 (1) | 58 (2) | 4.2 (6) | C(29) | -100 (8) | 253 (1) | 409 (2) | 4.7 (8) |
| C(6) | 228 (6) | 174 (1) | -10 (2) | 3.0 (6) | C(30) | -255 (8) | 229 (1) | 488 (2) | 6.2 (8) |
| C(7) | 420 (6) | -35 (1) | 187 (2) | 3.8 (6) | C(21') | 563 (5) | 12 (1) | 592 (1) | 2.0 (5) |
| C(8) | 255 (7) | -83 (1) | 154 (2) | 4.3 (6) | C(22') | 409 (6) | 7 (1) | 682 (2) | 2.5 (5) |
| C(9) | -69 (6) | -98 (1) | 32 (2) | 3.3 (6) | C(23') | 332 (6) | -45 (1) | 690 (2) | 2.6 (5) |
| C(10) | -239 (6) | -75 (1) | -49 (2) | 4.3 (7) | C(24') | 607 (5) | -67 (1) | 649 (1) | 1.2 (5) |
| C(1') | 564 (6) | 145 (1) | -141 (2) | 4.8 (7) | C(25') | 599 (6) | -120 (1) | 608 (2) | 2.6 (5) |
| C(2') | 403 (6) | 151 (1) | -229 (2) | 3.5 (6) | | | | | |
| C(3') | 301 (5) | 202 (1) | -231 (2) | 2.2 (5) | | | | | |
| C(4') | 606 (7) | 229 (1) | -195 (2) | 6.0 (8) | | | | | |
| C(5') | 567 (6) | 278 (1) | -156 (2) | 3.2 (5) | | | | | |

mined by a rapid scan at the calculated Bragg peak, and the rate of scanning (2θ) varied from 1° min^{-1} (less than 100 counts in the rapid scan) to 3° min^{-1} (more than 1000 counts during the rapid scan). Three standards were monitored after every 100 reflections during the course of the experiment, and their intensities showed only statistical variations. The 2734 measured intensities, which included standards, systematic absences and some duplicate data, were subsequently reduced to a set of 2220 reflections with $I > 0$. These reflections were assigned observational variations based on the formula: $\sigma^2(I) = S + (B_1 + B_2)(T_S/2T_B)^2 + (pI)^2$, where S , B_1 and B_2 are the scan and extremum background counts, T_S and T_B are the scan and individual background counting times ($T_B = T_S/4$ for all reflections), and $p = 0.04$ and represents the expected error proportional to the intensity (Busing & Levy, 1957). The intensities and their standard deviations were corrected for Lorentz and polarization effects and for the effect of absorption. The transmission factors ranged from 0.820 to 0.903. The data were placed on an approximate absolute scale by the method of Wilson (1942).

The parameters for the two independent Cu atoms were determined from a Patterson synthesis.

Two cycles of structure-factor Fourier calculations allowed the positioning of the remaining 56 nonhydrogen atoms in the asymmetric unit [R (all atoms included) = $\Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.28$]. Nine cycles of full-matrix least-squares refinement [minimizing the quantity $\Sigma w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$] with all atoms isotropic except for the two Cu atoms

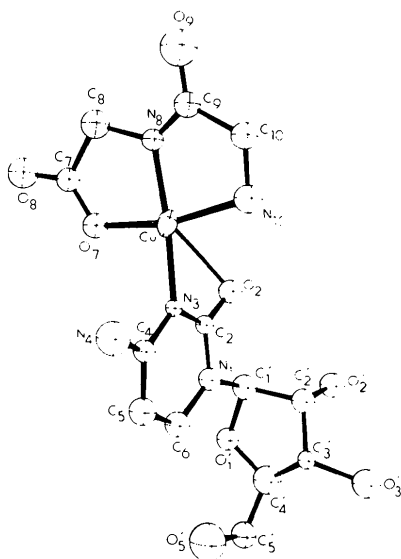


Fig. 1. A perspective view of the N(3),O(2)-bonded cytidine complex of glycyglycinatocopper(II). Molecule 1 is numbered as in this figure, and molecule 2 is numbered as 20 plus the number of the corresponding atom in molecule 1.

(which were treated anisotropically), led to final R values of 0.144 (all data) and 0.127 [the 1852 data with $F_o \geq 3\sigma(F_o)$]. In the final few cycles of refinement, 30 reflections were removed from the data set because they were ill-fit, apparently as a result of very high backgrounds during data collection. The final values for the weighted R index $\{[\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}\}$ and the goodness-of-fit $\{[\Sigma w(|F_o| - |F_c|)^2 / (NO - NV)]^{1/2}\}$, where $NO = 2190$ independent observations and $NV = 242$ variables were 0.121 and 2.5 respectively.*

Scattering factors for all atoms were taken from the compilation of Hanson, Herman, Lea & Skillman (1964). The real and imaginary parts of the scattering curves for all atoms were corrected for anomalous dispersion effects (Cromer & Liberman, 1970). Throughout the calculations we have assumed that the absolute configuration of the crystal is such that the molecular configuration of the sugar residues is D.

Final atomic parameters are collected in Table 1. The general numbering scheme is illustrated in Fig. 1. The numbering of the two independent complexes is as follows: (1) molecule 1 is numbered as in Fig. 1; (2) molecule 2 is numbered as 20 plus the number of the corresponding atom in molecule 1.

The structure factor and Fourier calculations were performed with the X-RAY 67 package of programs (Stewart, 1967); the least-squares refinements were performed with an extensively modified version of *ORFLS* (Busing, Martin & Levy, 1962); the absorption-correction program was *ORABS* (Wehe, Busing & Levy, 1962); best planes were computed with the program of Pippy & Ahmed (1968); the illustrations were prepared with the aid of *ORTEP* (Johnson, 1965). All other calculations were performed with locally written programs.

Results and discussion

Fig. 1 illustrates the general conformational features of the (glycyglycinato)(cytidine)copper(II) complex. The coordination geometry about the Cu^{II} atom is pseudo square pyramidal (4 + 1). The tridentate glycyglycinato dianion occupies three of the equatorial coordination sites with N(3) of cytidine completing the equatorial plane, mean $\text{Cu}-\text{N}(3) = 2.01(3) \text{ \AA}$. The exocyclic oxygen O(2) occupies one of the axial positions, mean $\text{Cu}-\text{O}(2) = 2.76(3) \text{ \AA}$; the $\text{Cu}-\text{O}(2)$ distance is long when compared to the occupation of axial positions by water or small anions

* A list of structure factors and tables of bond lengths, bond angles and best-planes calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32124 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

(Hodgson, 1977; Kistenmacher & Marzilli, 1976), but surely contributes significantly to the molecular stability and conformational properties. As we have noted in several instances (Szalda, Marzilli & Kistenmacher, 1975*a*; Kistenmacher, Szalda & Marzilli, 1975; Szalda, Marzilli & Kistenmacher, 1975*b*), the molecular features of the chelates of cytidine(cytosine) to Cu^{II} are essentially constant over the range of complexes studied. Furthermore, we have suggested that chelation may play an important role in the recognition of cytidine residues in polynucleotides by Cu^{II} . The chelation by cytidine(cytosine) is in marked contrast to the observation of a direct O(6)–metal interaction in 6-oxopurines. In only one case, (*N*-3,4-benzosalicylidene-*N'*,*N'*-dimethylethylenediamine)(theophyllinato)copper(II) (Szalda, Kistenmacher & Marzilli, 1976), has it been shown that a 6-oxopurine chelates to a metal center [$\text{Cu}-\text{N}(7) = 1.956(3)$ and $\text{Cu}-\text{O}(6) = 2.919(3)$ Å]. Thus while chelation is a rare phenomenon in 6-oxopurines, it appears to be the norm for cytidine(cytosine) with Cu^{II} .

While the general conformational features of the cytosine (Kistenmacher, Szalda & Marzilli, 1975) and the cytidine complexes of glycyglycinatocopper(II) are similar, there are several differences worthy of mention. (1) The dihedral angle between the six-atom pyrimidine framework and the equatorial plane is $68.1(3)^\circ$ in the cytosine complex, while it is $101(3)^\circ$ (mean) in the cytidine complex. (2) The deviation of O(2) from the six-atom pyrimidine plane is 0.19 Å in the cytosine complex, while it is only 0.02 Å (mean) in the cytidine complex. In this respect, the out-of-plane deviations of O(2) are 0.03 Å in the cytosine complex of (*N*-salicylidene-*N'*-methylethylenediamine)copper(II), and 0.01 and 0.02 Å in dichlorobis(cytosine)-copper(II) (Sundaralingam & Carrabine, 1971). Thus, a small out-of-plane deviation of O(2) is to be expected. (3) The Cu atom lies 0.36 Å (mean) out of the pyrimidine plane in the cytidine complex, while it is only 0.115 Å out of the plane in the cytosine complex. The deviation of the Cu leads to an angle between the Cu–N(3) vector and the pyrimidine plane of $10(2)^\circ$ (mean) in the cytidine complex and only $3.3(2)^\circ$ in the cytosine complex. (4) There is a slightly larger tetrahedral component to the equatorial plane in the cytidine complex than in the cytosine complex. (5) Many of the above features may be a result of the expansion of the

primary coordination sphere in the cytosine complex to $(4 + 2)$ via an intermolecular Cu–O(2) bond of $2.713(3)$ Å, while the cytidine complex is formally $(4 + 1)$.

The molecular conformations of the two independent complexes are nearly identical. The complexes are related by a local twofold axis parallel to *a*. We have deduced the form of the pseudosymmetry operation relating the two complexes by a linear least-squares regression analysis: $x' = 1.043x - 0.016$; $y' = -0.978y + 0.154$; $z' = -0.989z + 0.0453$. In each of the equations, all atoms from both complexes were included with unit weights, and the coefficient of determination was 0.99. This is a remarkably good fit considering that this is purely a local twofold, and not a crystallographic, symmetry operation.

The averaged bond lengths and angles for the two independent complexes have been deposited.* The high standard deviations preclude any detailed analysis, but in general the averaged parameters in the primary coordination sphere and in the glycyglycinato ligand are in good agreement with other determinations (Kistenmacher & Szalda, 1975; Kistenmacher, Szalda & Marzilli, 1975).

* See previous footnote.

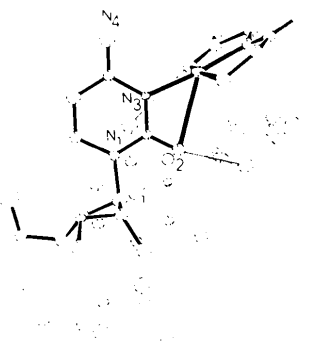


Fig. 3. A projection view of the molecular overlap in the columnar stacks along *a*. The view direction is along the normal to the mean plane of the pyrimidine rings. Note the positioning of the hetero-bonds N(1)–C(1') and C(4)–N(4) relative to the pyrimidine rings. Both complexes show essentially identical stacking patterns, and the mean stacking distances are 3.51 Å for molecule 1 and 3.42 Å for molecule 2.

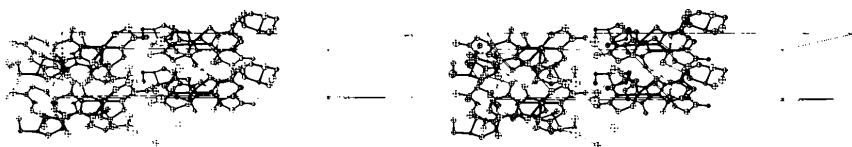


Fig. 2. A general stereo view of the crystal packing. The origin is at the lower-left, rear corner with $-a$ vertical, b horizontal and c toward the viewer. This view clearly illustrates the columnar stacking of the complexes along *a*.

The molecular dimensions and topology of the cytidine ligand are closely related to those in cytidine itself (Furberg, Petersen & Rømming, 1965). The glycosyl torsion angle is *anti* with a magnitude of $16(3)^\circ$ (mean) in the complex and $18.4(4)^\circ$ in free cytidine. Both sugars exhibit the common C(3') *endo* puckering and the conformation about the C(4')–C(5') bond is *gauche-gauche* in both ribose rings. The complexed cytidine residue even shows the close C(6)···O(5') contact [$3.22(5)$ Å (mean)] Å as Furberg *et al.* (1965) found in cytidine [$3.233(6)$ Å].

The crystal packing is composed of a large network of hydrogen bonds and a significant stacking of the complexes along the short *a* axis (Figs. 2 and 3).

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