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Structure of Bis(4-amino-1,2-dihydro-1-methyl-5-nitroso-2-oxo-6-pyrimidinolato-*O,N*)-diaquazinc(II) Dihydrate

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Abstract. $[Zn(C_5H_5N_4O_3)_2(H_2O)_2].2H_2O$, $M_r = 475.68$, triclinic, $P\bar{1}$, $a = 11.4430\ (6)$, $b = 9.5610\ (4)$, $c = 8.1430\ (2)$ Å, $\alpha = 102.1\ (1)$, $\beta = 94.1\ (1)$, $\gamma = 97.6\ (1)°$, $V = 858.7\ (4)$ Å^3, $Z = 2$, $D_m = 1.79\ (6)$, $D_x = 1.840$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 15.35$ cm^{-1}, $F(000) = 488$, room temperature, final $R = 0.042$ for 4280 observed reflections. The Zn^{II} ion is involved in a distorted octahedral coordination, in which the equatorial positions are occupied by two bidentate ligands through the nitrogen and oxygen atoms of the substituents in 5 and 6 positions, respectively. Two molecules of water are in the axial positions of the octahedron, whereas the other two are involved in the formation of hydrogen bonds.

Introduction. The study of transition-metal complexes with pyrimidine derivatives has received increasing attention in the last few years from both inorganic and biological points of view (Hodgson, 1977; Martin & Mariam, 1973), since it has been found that the metal ions play a vital role in the biochemistry of living systems and some of these complexes have shown chemotherapeutic effects (Rosenberg, 1971, 1973).

There are only a few crystallographic reports on 5-nitrosopyrimidine complexes (Romero-Molina, Martin-Ramos, López-González & Valenzuela-Calahorro, 1983; Ruiz-Valero, Monge, Gutiérrez-Puebla & Gutiérrez-Rios, 1983, 1984) and all of them are referred to metal complexes with 1,3-dimethyl-violuric acid. They show that this pyrimidine derivative is bound to metal ions, in bidentate form, through the oxygen and nitrogen atoms of the 6-oxide and 5-nitroso groups, respectively.

As a new example of this type of compound, we report in this paper the crystal structure of bis(4-amino-1,2-dihydro-1-methyl-5-nitroso-2-oxo-6-pyrimidinolato)diaquazinc(II) dihydrate.

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Experimental. Complex prepared by dissolving 4 mmol of zinc(II) acetate and 2 mmol of 4-amino-1-methyl-5-nitroso-2,6-dioxo-1,2,3,6-tetrahydropyrimidine in 200 ml of hot water. Some days later, red crystals appeared. Experimental data for determination of crystal structure collected at CNR Centro di Studio per la Cristallografia Strutturale of Pavia, Italy. Crystal $0.77 \times 0.64 \times 0.54$ mm. D_m pycnometrically (using acetone). Philips PW 1100 four-circle diffractometer. Accurate cell parameters from 32 high-angle (θ range 2–25°) reflections using locally improved version of Philips LAT routine, which allows fast and accurate determination of d spacings by determining the center of gravity of the reflections in a row of the reciprocal space passing through the origin only if their intensities exceed a predetermined counting threshold. ω-scan mode, scan width 2°, scan speed $0.1° s^{-1}$; 3 standard reflections monitored at 4 h intervals with max. intensity variation 5.2%; 5055 measured reflections in the range 2–30° ($h = 15$ to $-16, k = 13$ to $-13, l = 11$ to 0; max. $\sin\theta/\lambda = 0.703$ Å^{-1}), 775 of which $[I \le 5\sigma(I)]$ considered unobserved. Intensities corrected for Lorentz–polarization factor and absorption following semi-empirical method of North, Phillips & Mathews (1968) (max. and min. absorption corrections 1.1873 and 1.0016). Structure solved by finding positions of Zn, O(1), $H_2O(1)$ and N(8) atoms by Patterson techniques. Other non-hydrogen atoms found by subsequent Fourier maps. Full-matrix least-squares refinements on F ($ORFLS$; Busing, Martin & Levy, 1962) then carried out for non-hydrogen atoms. Atomic coordinates of hydrogen atoms calculated on the basis of geometrical considerations ($XANADU$; Roberts & Sheldrick, 1975) and checked on difference Fourier map; refined parameters: coordinates and anisotropic thermal parameters for non-H atoms and alternately scale factors and secondary anisotropic extinction coefficient [final value $= 4.2$ (2) $\times 10^{-4}$ following Coppens & Hamilton (1970)]. Final $R_{all} = 0.049$, $R_{obs} = 0.042$; $wR = 0.043$, each reflection given weight based on counting statistics, $w = 1/\sigma^2(F)$; max. and min. heights in final difference Fourier map 1.13 and -1.04 e Å^{-3}; max. Δ/σ for anisotropic extinction

Fig. 1. A perspective view of the molecule showing the atom numbering.

coefficients in final refinement cycle 1.870; for coordinates and anisotropic thermal parameters Δ/σ always lower than 1. $S = 0.781$. Atomic scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974). $PARST$ program (Nardelli, 1983) used for calculating molecular parameters; figures drawn with $ORTEP$II (Johnson, 1976).

Discussion. The stereochemistry of the complex is illustrated in Fig. 1, which also gives the atom numbering.

Table 1 contains the final atomic coordinates together with the equivalent isotropic temperature factors for non-H atoms. The intramolecular bond distances and angles are listed in Table 2.*

Zn coordination

The Zn atom is involved in octahedral coordination, with two bidentate 4-amino-1,2-dihydro-1-methyl-5-nitroso-2-oxopyrimidine-6-oxide ligands coordinated through the nitrogen [N(8) and N(81)] and oxygen

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* Lists of structure factors, coordinates of H atoms, anisotropic thermal parameters of non-H atoms, equations of least-squares planes with the deviation of the atoms from the planes and ring-puckering coordinates with the asymmetry parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42644 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Zn(1)	0.29538 (3)	0.19768 (3)	0.21718 (4)	1.88 (1)
O(1)	0.3255 (2)	0.3560 (2)	0.0756 (2)	2.27 (4)
C(2)	0.2499 (2)	0.4390 (2)	0.0908 (3)	1.80 (5)
N(3)	0.2611 (2)	0.5577 (2)	0.0229 (3)	2.12 (5)
C(4)	0.1829 (2)	0.6604 (2)	0.0505 (3)	2.40 (6)
N(5)	0.0886 (2)	0.6410 (2)	0.1387 (3)	2.50 (5)
C(6)	0.0669 (2)	0.5220 (3)	0.1998 (3)	2.11 (5)
C(7)	0.1461 (2)	0.4152 (2)	0.1801 (3)	1.80 (5)
N(8)	0.1394 (2)	0.2952 (2)	0.2393 (3)	2.09 (5)
C(9)	0.3609 (3)	0.5827 (3)	−0.0779 (4)	3.14 (8)
O(10)	0.2049 (2)	0.7680 (2)	−0.0080 (3)	3.92 (6)
N(11)	−0.0261 (2)	0.5027 (3)	0.2837 (3)	2.90 (6)
O(12)	0.0523 (2)	0.2560 (2)	0.3172 (3)	3.32 (6)
O(11)	0.2393 (2)	0.0451 (2)	0.3656 (2)	2.20 (4)
C(21)	0.3091 (2)	−0.0451 (2)	0.3684 (3)	1.67 (5)
N(31)	0.2845 (2)	−0.1553 (2)	0.4484 (2)	1.77 (4)
C(41)	0.3544 (2)	−0.2676 (2)	0.4397 (3)	1.86 (5)
N(51)	0.4585 (2)	−0.2581 (2)	0.3700 (3)	2.10 (5)
C(61)	0.4925 (2)	−0.1469 (2)	0.2996 (3)	1.83 (5)
C(71)	0.4190 (2)	−0.0370 (2)	0.2916 (3)	1.75 (5)
N(81)	0.4394 (2)	0.0790 (2)	0.2214 (3)	2.22 (4)
C(91)	0.1800 (2)	−0.1625 (3)	0.5426 (3)	2.55 (7)
O(101)	0.3166 (2)	−0.3720 (2)	0.4968 (3)	2.79 (5)
N(111)	0.5949 (2)	−0.1385 (3)	0.2345 (3)	2.77 (6)
O(121)	0.5348 (2)	0.1054 (2)	0.1601 (3)	3.23 (5)
H$_2$O(1)	0.3673 (2)	0.3517 (2)	0.4425 (3)	3.00
H$_2$O(2)	0.2187 (2)	0.0477 (2)	−0.0096 (2)	2.49
H$_2$O(3)	0.1854 (2)	0.2793 (2)	0.6836 (3)	3.68
H$_2$O(4)	0.0187 (2)	0.0890 (2)	−0.1943 (3)	3.73
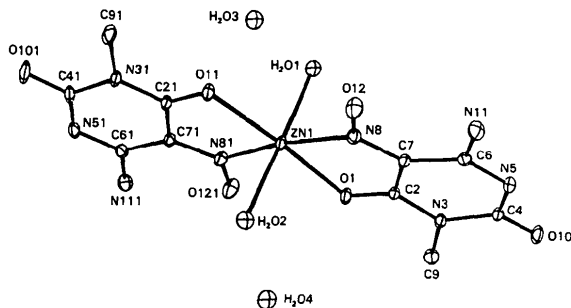
atoms [O(1) and O(11)] of the exocyclic substituents in 5 and 6 positions of the pyrimidine ring, respectively. The octahedron is completed by two molecules of water which occupy the axial positions in the coordination sphere.

The Zn—N and Zn—O lengths [2·123 (3), 2·124 (3) and 2·096 (3), 2·145 (3) Å] may be compared with the Zn—N and Zn—O distances of 2·06 and 2·05 Å, respectively, in the octahedral complex Zn(8-quinolinol)$_2$(H$_2$O)$_2$ (Merrit, Cady & Muudy, 1954). These values are also longer than those found in the complexes hexaaquairon(II) bis{tris[1,3-dimethyl-2,4,-5,6(1H,3H)-pyrimidinetetrone 5-oximato]ferrate(II)} dodecahydrate (Ruiz-Valero, Monge, Gutiérrez-Puebla & Gutiérrez-Rios, 1984) and diaquabis(1,3-dimethyl-5-nitroso-2,4-dioxo-1,2,3,4-tetrahydro-6-pyrimidinolato)copper(II) (Romero-Molina, Martin-Ramos, López-González & Valenzuela-Calahorro, 1983) in which the coordination mode of the pyrimidine derivative to Fe^{II} and Cu^{II} ions takes place in a similar way (N,O coordinated).

The large deviations of the angles O(1)—Zn—N(8), N(8)—Zn—O(11), O(11)—Zn—N(81) and N(81)—Zn—O(1) from the ideal octahedral values indicate a strong distortion in the geometry of this complex.

The ligand structure

The two pyrimidine rings are not equivalent and deviate slightly from planarity, the largest deviations from the least-squares planes, computed in both cases for the heterocyclic atoms, being 0·029 (3) Å for C(2) and 0·043 (2) Å for N(31). The dihedral angle defined by these two planes is 4·36 (9)°.

In spite of the crystallographic non-equivalence of the two pyrimidine rings, all the conclusions about the character of the bonds apply to both rings. The bond lengths C(2)—N(3), C(4)—N(5) and C(6)—N(5) [respectively 1·359 (3), 1·353 (4) and 1·336 (4) Å] are considerably shorter than the C(4)—N(3) bond, 1·409 (4) Å, showing appreciable double-bond character (Ladd, 1979). On the other hand, the C—O bond lengths are in agreement with those expected for a double bond, the C(2)—O(1) bond length being a little longer as this oxygen atom is involved in the coordination to the Zn^{II} ion. Likewise, the C(6)—N(11), C(7)—N(8) and N(8)—O(12) distances (see Table 2) indicate electronic delocalization.

The bond-length trend just described is in agreement with the conclusions reported for diaquabis-(1,3-dimethyl-5-nitroso-2,4-dioxo-1,2,3,4-tetrahydro-6-pyrimidinolato)copper(II) (Romero-Molina, Martin-Ramos, López-González & Valenzuela-Calahorro, 1983).

Molecular arrangement and hydrogen bonds

The packing scheme in the crystal is shown in Fig. 2.

The atoms participating in hydrogen-bond formation together with some relevant geometrical values are summarized in Table 3.
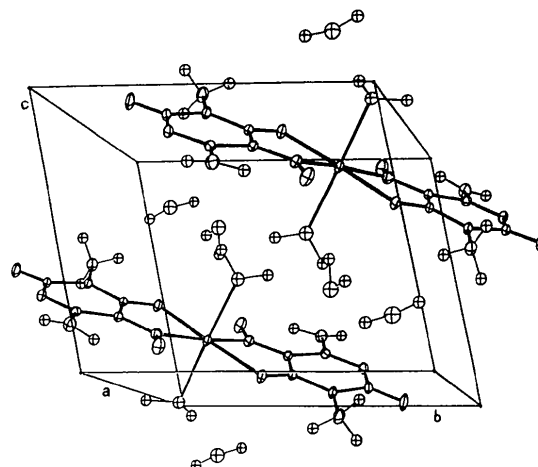
Table 2. *Bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses*

Zn(1)—O(1)	2·096 (3)	C(6)—N(11)	1·318 (4)
Zn(1)—N(8)	2·123 (3)	C(7)—N(8)	1·329 (3)
Zn(1)—O(11)	2·145 (3)	N(8)—O(12)	1·276 (3)
Zn(1)—N(81)	2·124 (3)	O(11)—C(21)	1·254 (3)
Zn(1)—H$_2$O(1)	2·130 (3)	C(21)—N(31)	1·360 (3)
Zn(1)—H$_2$O(2)	2·134 (3)	C(21)—C(71)	1·444 (3)
O(1)—C(2)	1·245 (3)	N(31)—C(41)	1·416 (3)
C(2)—N(3)	1·359 (3)	N(31)—C(91)	1·467 (4)
C(2)—C(7)	1·454 (4)	C(41)—N(51)	1·357 (3)
N(3)—C(4)	1·409 (4)	C(41)—O(101)	1·228 (3)
N(3)—C(9)	1·475 (4)	N(51)—C(61)	1·337 (3)
C(4)—N(5)	1·353 (4)	C(61)—C(71)	1·440 (4)
C(4)—O(10)	1·226 (4)	C(61)—N(111)	1·320 (3)
N(5)—C(6)	1·336 (4)	C(71)—N(81)	1·351 (3)
C(6)—C(7)	1·445 (4)	N(81)—O(121)	1·251 (3)

H$_2$O(1)—Zn(1)—H$_2$O(2)	178·0 (2)	C(7)—C(6)—N(11)	119·0 (3)
N(81)—Zn(1)—H$_2$O(2)	88·8 (2)	C(2)—C(7)—C(6)	118·6 (3)
N(81)—Zn(1)—H$_2$O(1)	93·1 (2)	C(6)—C(7)—N(8)	128·1 (4)
O(11)—Zn(1)—H$_2$O(2)	91·0 (1)	C(2)—C(7)—N(8)	113·2 (4)
O(11)—Zn(1)—H$_2$O(1)	89·6 (1)	Zn(1)—N(8)—C(7)	112·9 (3)
O(11)—Zn(1)—N(81)	77·1 (1)	C(7)—N(8)—O(12)	121·4 (4)
N(8)—Zn(1)—H$_2$O(2)	91·8 (2)	Zn(1)—N(8)—O(12)	125·2 (3)
N(8)—Zn(1)—H$_2$O(1)	96·3 (2)	Zn(1)—O(11)—C(21)	112·1 (2)
N(8)—Zn(1)—N(81)	170·6 (1)	O(11)—C(21)—C(71)	122·8 (3)
N(8)—Zn(1)—O(11)	93·6 (2)	O(11)—C(21)—N(31)	120·4 (4)
O(1)—Zn(1)—H$_2$O(2)	88·6 (1)	N(31)—C(21)—C(71)	116·8 (3)
O(1)—Zn(1)—H$_2$O(1)	90·5 (1)	C(21)—N(31)—C(91)	119·7 (3)
O(1)—Zn(1)—N(81)	111·4 (2)	C(21)—N(31)—C(41)	122·1 (3)
O(1)—Zn(1)—O(11)	171·6 (3)	C(41)—N(31)—C(91)	118·1 (3)
O(1)—Zn(1)—N(8)	78·0 (2)	N(31)—C(41)—O(101)	117·3 (4)
Zn(1)—O(1)—C(2)	112·0 (2)	N(31)—C(41)—N(51)	120·3 (3)
O(1)—C(2)—C(7)	122·7 (3)	N(51)—C(41)—O(101)	122·4 (4)
O(1)—C(2)—N(3)	120·7 (4)	C(41)—N(51)—C(61)	120·3 (4)
N(3)—C(2)—C(7)	116·6 (3)	N(51)—C(61)—N(111)	119·3 (4)
C(2)—N(3)—C(9)	119·0 (3)	N(51)—C(61)—C(71)	121·3 (4)
C(2)—N(3)—C(4)	122·1 (3)	C(71)—C(61)—N(111)	119·3 (3)
C(4)—N(3)—C(9)	118·9 (3)	C(21)—C(71)—C(61)	118·6 (3)
N(3)—C(4)—O(10)	116·9 (4)	C(61)—C(71)—N(81)	128·3 (4)
N(3)—C(4)—N(5)	121·3 (3)	C(21)—C(71)—N(81)	113·1 (4)
N(5)—C(4)—O(10)	121·8 (4)	Zn(1)—N(81)—C(71)	114·2 (3)
C(4)—N(5)—C(6)	120·1 (4)	C(71)—N(81)—O(121)	120·2 (4)
N(5)—C(6)—N(11)	119·9 (4)	Zn(1)—N(81)—O(121)	125·5 (3)
N(5)—C(6)—C(7)	121·1 (3)		

Fig. 2. Packing of the molecule.

Table 3. *Distances (Å) and angles (°) in interactions of the type* $D-H\cdots A$

D	H	A	$H\cdots A$	$D-H\cdots A$
N(11)	H(112)	O(12)	1·95 (3)	134 (2)
N(111)	H(1B2)	O(121)	1·99 (3)	128 (2)
H₂O(3)	HO(31)	O(11)	2·49 (2)	127 (2)
H₂O(2)	HO(21)	H₂O(4)	1·92 (2)	168 (2)
H₂O(3)	HO(31)	H₂O(1)	2·20 (2)	144 (2)
H₂O(2)	HO(22)	O(10ⁱ)	1·64 (2)	173 (1)
N(111)	H(1B1)	H₂O(3ⁱⁱ)	2·39 (3)	148 (3)
H₂O(1)	HO(12)	N(51ⁱⁱ)	1·67 (2)	160 (2)
H₂O(3)	HO(32)	H₂O(4ⁱⁱⁱ)	2·36 (2)	135 (2)
H₂O(4)	HO(41)	O(12ⁱᵛ)	2·38 (2)	154 (2)
H₂O(4)	HO(41)	O(11ⁱᵛ)	2·56 (2)	124 (2)
H₂O(4)	HO(42)	N(5ᵛ)	2·08 (2)	162 (2)
H₂O(4)	HO(42)	O(10ᵛ)	2·64 (2)	143 (2)
N(11)	H(111)	H₂O(3ᵛⁱ)	2·09 (3)	176 (2)
N(111)	H(1B2)	H₂O(2ᵛⁱⁱ)	2·41 (2)	126 (2)
H₂O(1)	HO(11)	H₂O(1ᵛⁱⁱⁱ)	1·86 (2)	157 (2)

Equivalent positions: (i) $x, y-1, z$; (ii) $1-x, \bar{y}, 1-z$; (iii) $x, y, 1+z$; (iv) $\bar{x}, \bar{y}, z$; (v) $\bar{x}, 1-y, z$; (vi) $\bar{x}, 1-y, 1-z$; (vii) $1-x, \bar{y}, z$; (viii) $x, 1+y, z$.

The intramolecular hydrogen bonds N(11)—H(112)···O(12) and N(111)—H(1B2)···O(121) could explain the appearance of one signal for the resonance of each aminic proton in the ¹H NMR spectrum of this complex dissolved in Me_2SOd_6 (Moreno-Carretero, 1983).

On the other hand, it is clear that the difference found between the Zn—O(11) and Zn—O(1) distances is caused by the hydrogen-bond interactions between O(11) and H₂O(3); furthermore, this could explain why the C(21)—O(11) bond length is slightly longer than the C(2)—O(1) distance.

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Structure of Hexakis(pyridine *N*-oxide)cobalt(II) Perchlorate by Neutron Diffraction at 90 K

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Abstract. $[Co(C_5H_5NO)_6](ClO_4)_2$, $M_r = 828·4$, rhombohedral, $R\bar{3}$, $a = 12·317$ (7), $c = 18·827$ (10) Å, $V = 2473·5$ Å³, $Z = 3$, $D_x = 1·668$, $D_m = 1·62$ g cm⁻³ (room temperature), $\lambda = 1·271$ Å, $\mu = 1·77$ cm⁻¹, $T = 90$ K, final $R(F^2) = 0·034$ for 1309 independent observed reflections. The $[Co(C_5H_5NO)_6]^{2+}$ ion possesses a nearly perfect octahedral coordination geometry with Co—O = 2·083 (1) Å and O—Co—O = 89·77 (4)°. The analysis reveals that a small amount of the pyridine *N*-oxide ligand (~5%) is displaced by *N,N*-dimethylformamide (DMF) solvent molecules, so that the chemical formula for the crystal examined is more appropriately written as $[Co(C_5H_5NO)_{5.7}(DMF)_{0.3}](ClO_4)_2$.