by 12 (4) and 10 (4)° out of their pyridine planes. The dihedral angles between the planes of the pyridine rings and the square plane around Pt are both 126 (3)°.

There are no abnormally short distances. The crystal is built up of discrete molecules of $PtCl_2$(vinylpyridine)$_2$ with adjacent molecules held by van der Waals forces.

This work was supported by the Polish Academy of Sciences.

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The Structures of Tetraaqua(uracil-6-carboxylato)zinc(II) Monohydrate (*A*) and Tetraaqua(uracil-6-carboxylato)nickel(II) Monohydrate (*B*)

BY ANASTAS KARIPIDES AND BARBARA THOMAS

Department of Chemistry, Miami University, Oxford, OH 45056, *USA*

(*Received* 5 *August* 1985; *accepted* 27 *June* 1986)

Abstract. Compound (*A*): $[Zn(C_5H_2N_2O_4)(H_2O)_4]$.$H_2O$, $M_r = 309{\cdot}54$, triclinic, $P\bar{1}$, $a = 7{\cdot}243\ (4)$, $b = 8{\cdot}390\ (3)$, $c = 10{\cdot}105\ (4)$ Å, $\alpha = 80{\cdot}10\ (3)$, $\beta = 109{\cdot}23\ (3)$, $\gamma = 113{\cdot}69\ (3)°$, $V = 530{\cdot}4$ Å^3, $Z = 2$, $D_m = 1{\cdot}94\ (2)$, $D_x = 1{\cdot}938$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 24{\cdot}3$ cm^{-1}, $F(000) = 316$, $T \sim 293$ K, final $R = 0{\cdot}036$ for 3151 observed unique reflections. Compound (*B*): $[Ni(C_5H_2N_2O_4)(H_2O)_4]$.$H_2O$, $M_r = 302{\cdot}86$, triclinic, $P\bar{1}$, $a = 7{\cdot}240\ (3)$, $b = 8{\cdot}298\ (3)$, $c = 10{\cdot}076\ (4)$ Å, $\alpha = 80{\cdot}11\ (3)$, $\beta = 109{\cdot}64\ (3)$, $\gamma = 114{\cdot}38\ (3)°$, $V = 518{\cdot}9$ Å^3, $Z = 2$, $D_m = 1{\cdot}93\ (2)$, $D_x = 1{\cdot}938$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 19{\cdot}1$ cm^{-1}, $F(000) = 312$, $T \sim 293$ K, final $R = 0{\cdot}036$ for 3566 observed unique reflections. In each of these isomorphous structures the bidentate uracil-6-carboxylate dianion binds each metal ion through the carboxylate group and the deprotonated adjacent pyrimidine nitrogen atom. The coordination polyhedron geometry is close to 'octahedral'. The pyrimidine rings are stacked in pairs with a 3·20 Å separation.

Introduction. Uracil-6-carboxylic acid or orotic acid* is an important naturally occurring pyrimidine derivative, which has the potential of serving as a polydentate ligand. Because of possible biological significance there has been interest in the variability in the modes of binding of a given nucleic acid constituent with different metal ions (Hodgson, 1977; Tu & Heller, 1974; Pezzano & Podo, 1980). As part of our studies in this area we have determined the crystal structures of the Zn^{2+} and Ni^{2+} 1:1 salts of orotic acid. After completion of our structural investigations we discovered that the structure of the isomorphous nickel compound had been reported by Sabat, Zglinska & Jeżowska-Trzebiatowska (1980). However, because our determination differs in certain respects concerning the data collection, the details of the structure of the Ni^{II} complex are included in this paper as deposited items.*

Experimental. Both (*A*) and (*B*) were prepared from the reaction of the corresponding metal carbonate with a hot (nearly boiling) aqueous solution of uracil-6-carboxylic acid. In each instance after evolution of CO_2 the hot solutions were quickly filtered to remove the excess metal carbonate. Colorless crystals of (*A*) and green crystals of (*B*) formed readily upon slow evaporation. Crystal size: (*A*) 0·25 × 0·25 × 0·50 mm; (*B*) 0·32 × 0·32 × 0·45 mm. Crystal densities measured by flotation in iodobenzene/iodomethane mixtures. Lattice parameters in each case obtained from 15 reflections ($2\theta > 30°$) at 293 ± 1 K. Intensity data [$\sin\theta/\lambda$ max. 0·7078 (*A*), 0·7425 Å^{-1} (*B*)]

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* 1,2,3,6-Tetrahydro-2,6-dioxo-4-pyrimidinecarboxylic acid.

* Lists of structure factors, anisotropic thermal parameters and hydrogen-bonding parameters for both crystals as well as fractional coordinates and bond distances/angles for the nickel complex have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43192 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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collected on a Nicolet diffractometer equipped with a graphite monochromator using a $\theta/2\theta$ scan technique. Six check reflections measured every 300 reflections showed no decay in intensity. Index range for both crystals: h −10 to 9; k −11 to 11; l 0 to 14. Total number of unique reflections measured for (*A*) was 3151 and for (*B*) 3566. Estimated standard deviations calculated as $\sigma(I) = [C + R^2B]$, where C = total integrated peak count, B = total background count, R = ratio of the scan time for the peak to the scan time for the background. $\sigma(F)$ calculated from $\sigma(F) = \{[\sigma(F_o)]^2 + (0{\cdot}02F_o)^2\}^{1/2}$ where $\sigma(F_o)$ is $(2F_o)^{-1}(\mathrm{Lp})^{-1}\sigma(I)$. For both crystals all reflections had $F_o > \sigma(F_o)$ and no reflections were taken as unobserved. Absorption and secondary-extinction corrections were not applied. Both structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures. Hydrogen atoms were located from difference maps; H parameters were not refined. Scattering factors and anomalous-dispersion corrections were from *International Tables for X-ray Crystallography* (1974). All calculations were performed on an IBM 4341 using established programs (Karipides, 1979). Anisotropic refinement (on F) of all non-hydrogen atoms (154 parameters) converged to $R = 0{\cdot}036$; $wR = 0{\cdot}046$ for (*A*) and $R = 0{\cdot}036$; $wR = 0{\cdot}045$ for (*B*), $w = 1/\sigma^2(F)$; maximum shift/e.s.d. in final least-squares cycle was 0·02 for both (*A*) and (*B*). Goodness-of-fit: for (*A*) 1·60 and for (*B*) 1·46. Maxima and minima in the final difference Fourier maps were: for (*A*) 0·49, −0·85 and for (*B*) 0·49, −0·78 e Å^{-3}. Final atom coordinates and equivalent isotropic thermal parameters are given in Table 1.

Table 1. *Fractional coordinates* (×10^4 *for non*-H *atoms;* ×10^3 *for* H *atoms) and equivalent isotropic temperature factors with e.s.d.'s for* $[Zn(C_5H_2N_2O_4)(H_2O)_4].H_2O$

$B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$, where the anisotropic thermal parameters (β_{ij}) are defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Isotropic thermal parameters for H atoms were fixed at 5·0 Å^2.

	x	y	z	B_{eq}(Å^2)
Zn	2535·6 (4)	3465·9 (3)	1836·6 (2)	1·82 (2)
O(1)	2359 (3)	1236 (2)	1098 (2)	2·20 (5)
O(2)	2559 (3)	3555 (2)	5156 (2)	2·22 (4)
O(3)	2133 (3)	−1500 (2)	1659 (2)	3·18 (8)
O(4)	2675 (3)	−1782 (2)	6872 (1)	2·27 (5)
O(5*w*)	2592 (4)	5474 (2)	2768 (2)	3·39 (8)
O(6*w*)	−903 (3)	2660 (2)	959 (2)	2·20 (5)
O(7*w*)	5976 (2)	4499 (2)	2498 (2)	2·14 (4)
O(8*w*)	2660 (3)	4846 (3)	−55 (2)	3·10 (7)
O(9*w*)	−3536 (4)	−1501 (4)	1241 (2)	5·50 (10)
N(1)	2392 (3)	1772 (2)	3608 (2)	1·57 (4)
N(3)	2585 (3)	864 (2)	5962 (2)	1·70 (4)
C(2)	2515 (3)	2134 (2)	4893 (2)	1·53 (6)
C(4)	2545 (3)	−759 (2)	5825 (2)	1·63 (6)
C(5)	2354 (3)	−1114 (2)	4442 (2)	1·81 (7)
C(6)	2318 (3)	174 (2)	3419 (2)	1·52 (6)
C(7)	2252 (3)	−67 (3)	1946 (2)	1·87 (6)
H1(O5*w*)	246	659	251	
H2(O5*w*)	228	501	364	
H1(O6*w*)	−134	204	14	
H2(O6*w*)	−164	198	161	
H1(O7*w*)	664	367	289	
H2(O7*w*)	642	525	325	
H1(O8*w*)	181	552	−54	
H2(O8*w*)	317	470	−78	
H1(O9*w*)	−325	−144	37	
H2(O9*w*)	−497	−240	108	
H(N2)	282	124	687	
N(C3)	217	−244	432	

Discussion. The Zn^{II} and Ni^{II} compounds are isomorphous and a view of the molecular structure is shown in Fig. 1. Bond distances and angles are presented in Table 2.

The structures consist of isolated $M(C_5H_2N_2O_4)(H_2O)_4$ formula units. Each metal ion is coordinated to four water molecules, a carboxylate oxygen and the adjacent deprotonated pyrimidine nitrogen atom forming an essentially planar five-membered chelate ring. The pyrimidine exocyclic oxygen atoms are not involved in metal ion binding. The slightly irregular sixfold coordination polyhedron in each structure resembles an octahedron, although as

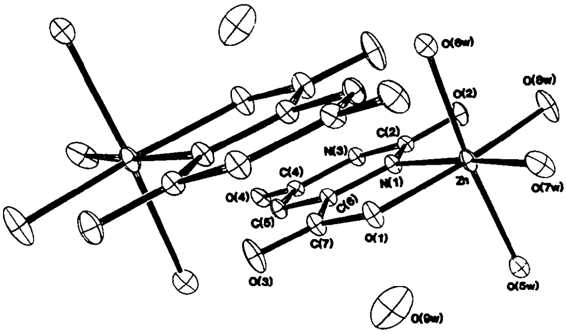

Fig. 1. A view of the unit-cell contents of (*A*) showing the atom-numbering scheme, mode of ligand–Zn^{2+} binding, and coordination polyhedron.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s for* $[Zn(C_5H_2N_2O_4)(H_2O)_4].H_2O$

Zn—N(1)	2·089 (2)	C(4)—O(4)	1·245 (2)
Zn—O(1)	2·073 (2)	C(4)—N(3)	1·381 (2)
Zn—O(6*w*)	2·201 (2)	C(4)—C(5)	1·429 (3)
Zn—O(7*w*)	2·185 (2)	C(5)—C(6)	1·363 (3)
Zn—O(8*w*)	2·066 (2)	C(6)—N(1)	1·364 (2)
Zn—O(5*w*)	2·047 (2)	C(6)—C(7)	1·519 (3)
C(2)—O(2)	1·251 (2)	C(7)—O(3)	1·247 (2)
C(2)—N(1)	1·351 (2)	C(7)—O(1)	1·261 (2)
C(2)—N(3)	1·384 (2)		

C(6)—N(1)—C(2)	118·8 (2)	O(5*w*)—Zn—O(8*w*)	94·0 (1)
N(1)—C(2)—N(3)	118·1 (2)	O(5*w*)—Zn—O(1)	172·9 (2)
O(2)—C(2)—N(1)	123·0 (2)	O(5*w*)—Zn—N(1)	94·4 (1)
O(2)—C(2)—N(3)	118·8 (2)	O(5*w*)—Zn—O(7*w*)	89·5 (1)
C(4)—N(3)—C(2)	125·1 (2)	O(5*w*)—Zn—O(6*w*)	89·5 (1)
N(3)—C(4)—C(5)	115·2 (2)	O(8*w*)—Zn—O(1)	92·9 (2)
O(4)—C(4)—N(3)	119·5 (5)	O(8*w*)—Zn—N(1)	171·7 (2)
O(4)—C(4)—C(5)	125·3 (5)	O(8*w*)—Zn—O(7*w*)	88·0 (1)
C(6)—C(5)—C(4)	118·1 (2)	O(8*w*)—Zn—O(6*w*)	85·3 (1)
N(1)—C(6)—C(5)	124·7 (2)	O(1)—Zn—N(1)	78·8 (1)
N(1)—C(6)—C(7)	114·2 (2)	O(1)—Zn—O(7*w*)	92·6 (1)
C(5)—C(6)—C(7)	121·1 (2)	O(1)—Zn—O(6*w*)	89·23 (1)
O(3)—C(7)—O(1)	124·5 (2)	N(1)—Zn—O(7*w*)	92·2 (1)
O(3)—C(7)—C(6)	119·1 (2)	N(1)—Zn—O(6*w*)	94·6 (1)
O(1)—C(7)—C(6)	116·4 (2)	O(6*w*)—Zn—O(7*w*)	173·1 (1)

a result of steric hindrance, the bond angles at the metal sites in each chelate ring of 78·8 (1) (Zn) and 80·4 (1)° (Ni) represent significant departures from the idealized angles. The Zn—O bond distances are uniformly longer than the corresponding Ni—O lengths. The pyrimidine ring is planar and the geometry of the ligand in each compound is consistent with that found in other derivatives containing the orotate(2−) ion (Sabat, Zglinska & Jeżowska-Trzebiatowska, 1980; Mutikainen & Lumme, 1980; Takusagawa & Shimada, 1973; Solbakk, 1971). The dihedral angles between the pyrimidine ring and chelate ring planes are 4·3 and 4·8° in the Zn and Ni compounds, respectively.

For each compound the crystal structure is dominated by an extensive array of hydrogen bonds involving all hydrogen atoms bound to non-carbon atoms except for H2(O9*w*) from the lone lattice water molecule, O(9*w*). Included in this scheme in each is the rather short intramolecular hydrogen bond, O(5*w*)···O(2) of 2·662 (Zn) and 2·659 Å (Ni).

The familiar base stacking patterns found in most pyrimidine structures is also retained in these metal complexes (Bugg, Thomas, Sundaralingham & Rao, 1971). The uracil moieties are stacked parallel with the N(3) atom of one base positioned approximately over the center of an adjacent ring, which is related to the first by an inversion center. Interplanar spacing between these stacked bases is 3·20 Å.

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Acta Cryst. (1986). C**42**, 1707–1711

Complexes of 2,2′-Bipyridine (bpy) and 1,10-Phenanthroline (phen) with Platinum(II). Structures of $[Pt^{II}(bpy)_{1.3}(phen)_{0.7}](NO_3)_2.0\cdot3H_2O$ and $[Pt^{II}(bpy)_2](NO_3)_2.H_2O$

BY ALAN HAZELL

*Institute of Chemistry, Aarhus University, DK-*8000 *Århus C, Denmark*

AND OLE SIMONSEN AND OLE WERNBERG

*Department of Chemistry, Odense University, DK-*5230 *Odense M, Denmark*

(*Received* 28 *April* 1986; *accepted* 4 *July* 1986)

Abstract. (1) $[Pt(C_{10}H_8N_2)_{1.3}(C_{12}H_8N_2)_{0.7}]$-$(NO_3)_2.0\cdot3H_2O$, $M_r = 653\cdot7$, monoclinic, $C2/c$, $a = 19\cdot522$ (4), $b = 15\cdot511$ (3), $c = 7\cdot078$ (3) Å, $\beta = 101\cdot56$ (3)°, $Z = 4$, $V = 2100$ (1) Å^3, $D_m = 2\cdot09$, $D_x = 2\cdot067$ (1) Mg m^{-3}, $F(000) = 1261\cdot6$, Mo $K\alpha$ ($\lambda = 0\cdot71069$ Å), $\mu = 6\cdot80$ (3) mm^{-1}, room temperature. $R = 0\cdot038$ for 1161 reflexions [$I > 3\sigma(I)$] and 161 variables. (2) Bis(2,2′-bipyridine)platinum(II) dinitrate monohydrate, $[Pt(C_{10}H_8N_2)_2](NO_3)_2.H_2O$, $M_r = 649\cdot5$, monoclinic, $C2/c$, $a = 19\cdot297$ (5), $b = 15\cdot502$ (4), $c = 7\cdot093$ (2) Å, $\beta = 101\cdot70$ (1)°, $Z = 4$, $V = 2078$ (1) Å^3, $D_x = 2\cdot076$ (1) Mg m^{-3}, $F(000) = 1256$, Mo $K\alpha$ ($\lambda = 0\cdot71069$ Å), $\mu = 6\cdot88$ (3) mm^{-1}, room temperature. $R = 0\cdot045$ for 3653 reflexions [$I > 3\sigma(I)$] and 168 variables. Mean Pt—N distances are 2·013 (6) Å for (1) and 2·026 (3) Å for (2). In both cases the overcrowding of the ligands is relieved by a tetrahedral distortion of PtN_4 [the angle between the planes through PtN_2 is 23·0 (4)° for (1) and 24·0 (3)° for (2)] and by distortion of the ligands [the angle between the best planes through the ligands is 31·8° for (1) and 34·5° for (2)]. The water molecules are in the plane of the bipyridine groups and close to the acid hydrogens, C(3)—O is 3·226 (8) Å for (2).

Introduction. The photochemical properties of transition metal–polypyridine complexes has led to their possible use in the conversion and storage of solar energy. Postulated mechanisms for their reaction with OH$^-$ have been the subject of much, often acrimonious,

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