

Discussion. Final atomic parameters, bond lengths and angles are given in Tables 1 and 2. The structure consists of polymeric two-dimensional sheets, with *syn-anti* acetate bridges connecting tetrahedrally coordinated Zn atoms (Fig. 1). The geometry of the coordination and of the acetate bridges is very similar to that found in the orthorhombic form, in which the bridges connect the Zn atoms into a three-dimensional network rather than two-dimensional sheets (Capilla & Aranda, 1979). Neither of these observed structures is consistent with the proposal of Johnson, Powell & Cannon (1981).

There is no covalent bonding between sheets, the acetate methyl groups protruding from them on each side (Fig. 2).

A similar sheet structure is observed for zinc(II) propionate (Goldschmied, Rae & Stephenson, 1977). By contrast, zinc(II) 2-chlorobenzoate forms polymeric chains with pairs of *syn-syn* bridges linking Zn atoms (Nakacho, Misawa, Fujiwara, Wakahara & Tomita, 1976); a different type of polymeric chain is found for zinc(II) benzoate (Guseinov, Musaev, Usubaliev, Amiraslanov & Mamedov, 1984) and zinc(II) crotonate (Clegg, Little & Straughan, 1986), in which Zn₂-(carboxylate)₂⁺ binuclear units with three *syn-syn* bridges are connected by single *syn-anti* carboxylates. Thus anhydrous zinc(II) carboxylates have been

observed with one-, two- and three-dimensional polymeric structures of different types, with the acetate existing in (at least) two forms.

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References

- CAPILLA, A. V. & ARANDA, R. A. (1979). *Cryst. Struct. Commun.* **8**, 795–798.
- CLEGG, W., LITTLE, I. R. & STRAUGHAN, B. P. (1986). *Acta Cryst.* **C42**, 919–920.
- GOLDSCHMIED, E., RAE, A. D. & STEPHENSON, N. C. (1977). *Acta Cryst.* **B33**, 2117–2120.
- GUSEINOV, G. A., MUSAEV, F. N., USUBALIEV, B. T., AMIRASLANOV, I. R. & MAMEDOV, KH. S. (1984). *Koord. Khim.* **10**, 117–122.
- International Tables for X-ray Crystallography* (1974). Vol. 1V, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOHNSON, M. K., POWELL, D. B. & CANNON, R. D. (1981). *Spectrochim. Acta Part A*, **37**, 399–404.
- NAKACHO, Y., MISAWA, T., FUJIWARA, T., WAKAHARA, A. & TOMITA, K. (1976). *Bull. Chem. Soc. Jpn.*, **49**, 58–61.
- NIEKERK, J. N. VAN, SCHOENING, F. R. L. & TALBOT, J. H. (1953). *Acta Cryst.* **6**, 720–723.
- SHELDRIK, G. M. (1985). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Revision 5. Univ. of Göttingen.

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Structure of *cis*-Dichlorobis(4-vinylpyridine)platinum(II)

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Abstract. [PtCl₂(C₇H₇N)₂], *M_r* = 476.3, monoclinic, space group *P*2₁/*c*, *a* = 13.709 (4), *b* = 13.359 (4), *c* = 11.739 (4) Å, β = 133.72 (5)°, *V* = 1553.8 (9) Å³, *Z* = 4, *D_x* = 2.04, *D_m* = 2.00 (5) Mg m⁻³, Mo *K*α, λ = 0.71069 Å, μ = 9.8 mm⁻¹, *F*(000) = 896, *T* = 294 (2) K, *R* = 0.059 for 2034 observed counter reflections. The Pt atom is coordinated to two N and two Cl atoms at the corners of a slightly distorted square with *cis* configuration. The Pt–Cl distances are 2.278 (7) and 2.301 (7) Å. The 4-vinylpyridine ligand is bonded to Pt through the N atom, Pt–N 1.969 (19) and 1.988 (23) Å.

Introduction. Since the discovery of the antitumour activity of Pt compounds, the importance of platinum metal has markedly increased in bio-inorganic chemistry. As studies of the structure–cytostatic activity

relationship show, only Pt complexes with *cis* configuration may afford potential drugs. Because *cis-trans* isomerization often occurs among complexes of pyridine derivatives, the precise determination of the configuration is necessary for the correlation between molecular structure and pharmacological activity.

As part of a programme directed towards the structural investigation of Pt^{II} and Pd^{II} complexes with pyridine derivatives, we present here the crystal structure of the title complex, obtained and characterized as described elsewhere (Kuduk-Jaworska, 1985).

Experimental. Yellow crystals, dimensions 0.12 × 0.14 × 0.20 mm; *D_m* by flotation in CCl₄/1,2-dibromoethane, monoclinic from Weissenberg photographs; Syntex *P*2₁ computer-controlled four-circle

diffractometer, Mo K α radiation, scintillation counter, graphite monochromator, cell parameters by least squares from setting angles of 15 reflections with $14 \leq 2\theta \leq 23^\circ$ measured on the diffractometer; 2740 independent reflections measured; $2\theta_{\max} = 45^\circ$; variable θ - 2θ scan rate, 2.0 - $29.3^\circ \text{ min}^{-1}$ (depending on intensity); two standards measured every 50 reflections, variation in their intensities $\pm 4\%$; corrections for Lorentz and polarization effects, but not for extinction; calculations performed on a NOVA 1200 computer with programs supplied by Syntex (1976), scattering factors from *International Tables for X-ray Crystallography* (1974); for structure solution and refinement 2034 amplitudes with $F \geq 8\sigma(F)$ retained, h 0 \rightarrow 16, k 0 \rightarrow 15, l -13 \rightarrow 10, Patterson synthesis and difference-Fourier methods; full-matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$; $w = 1/\sigma^2(F)$; H atoms included in geometrically calculated positions (with $B = 6.0 \text{ \AA}^2$), non-H atoms with anisotropic thermal parameters, an absorption correction following the *DIFABS* procedure (Walker & Stuart, 1983) was applied to isotropically refined data; max. and min. absorption factors 1.302 and 0.628, respectively; $(\Delta/\sigma)_{\max} = 0.1$; residual electron density in final difference map within -0.20 and 0.30 e \AA^{-3} ; $R = 0.059$, $wR = 0.069$, $S = 5.3$.

Discussion. The positional parameters are reported in Table 1,* the relevant bond distances and angles in Table 2. Fig. 1 shows a view of the complex and the atom numbering.

The environment of the Pt atom is an approximate square. The two Cl atoms and the 4-vinylpyridine N atoms are coordinated to Pt in a *cis* geometry. The Pt atom is displaced from the coordination plane by 0.031 (1) \AA . The Pt-Cl and Pt-N distances are close to those published in the literature for related complexes (Rochon, Kong & Melanson, 1980).

Both pyridine rings are planar, with no atom deviating from the least-squares planes through the six atoms by more than 0.02 (3) \AA . The vinyl C(17) and C(27) atoms are 0.23 (3) and 0.18 (6) \AA out of these planes. The bond lengths and angles in the 4-vinylpyridine ligand are similar to those observed in a variety of metal complexes of pyridine and its derivatives (Navarro-Ranninger, Martínez-Carrera & García-Blanco, 1985). The pyridine rings have C-C distances in the range 1.35 (4) to 1.37 (3) \AA and C-N lengths from 1.35 (2) to 1.40 (3) \AA . The vinyl C-C bonds are 1.31 (4) and 1.35 (4) \AA . The vinyl groups are rotated

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2) with e.s.d.'s in parentheses*

$$B_{\text{eq}} = \frac{1}{3}(B_{11} + B_{22} + B_{33}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Pt	0.07844 (9)	0.09539 (5)	0.20647 (9)	3.05 (5)
Cl(1)	0.2991 (6)	0.0427 (4)	0.3959 (6)	4.1 (4)
Cl(2)	0.0014 (7)	-0.0568 (4)	0.2029 (7)	5.1 (5)
N(1)	-0.1108 (18)	0.1447 (9)	0.0551 (19)	4.0 (14)
N(2)	0.1383 (16)	0.2281 (12)	0.2019 (18)	3.5 (14)
C(11)	-0.2181 (23)	0.0954 (16)	-0.0850 (24)	4.1 (18)
C(12)	-0.3476 (23)	0.1296 (15)	-0.1793 (26)	3.9 (19)
C(13)	-0.3800 (22)	0.2096 (14)	-0.1378 (24)	3.6 (17)
C(14)	-0.2756 (22)	0.2592 (14)	-0.0029 (22)	3.6 (17)
C(15)	-0.1479 (23)	0.2248 (14)	0.0882 (22)	3.7 (17)
C(16)	-0.5215 (24)	0.2424 (15)	-0.2439 (28)	4.5 (21)
C(17)	-0.5587 (26)	0.3289 (22)	-0.2306 (32)	6.3 (28)
C(21)	0.0886 (23)	0.2750 (15)	0.0656 (24)	4.1 (19)
C(22)	0.1226 (25)	0.3684 (16)	0.0577 (25)	4.7 (20)
C(23)	0.2158 (24)	0.4260 (14)	0.1965 (29)	4.8 (21)
C(24)	0.2701 (24)	0.3804 (15)	0.3416 (26)	4.5 (20)
C(25)	0.2313 (23)	0.2856 (15)	0.3352 (25)	4.4 (19)
C(26)	0.2564 (30)	0.5252 (18)	0.1972 (33)	7.0 (27)
C(27)	0.3300 (41)	0.5896 (20)	0.3193 (43)	10.4 (43)

Table 2. *Bond distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses*

Pt-Cl(1)	2.301 (7)	Pt-N(1)	1.988 (23)
Pt-Cl(2)	2.278 (7)	Pt-N(2)	1.969 (19)
N(1)-C(11)	1.400 (27)	N(2)-C(21)	1.383 (28)
N(1)-C(15)	1.352 (23)	N(2)-C(25)	1.381 (26)
C(11)-C(12)	1.368 (44)	C(21)-C(22)	1.358 (35)
C(12)-C(13)	1.369 (37)	C(22)-C(23)	1.415 (32)
C(13)-C(14)	1.365 (29)	C(23)-C(24)	1.440 (35)
C(14)-C(15)	1.354 (42)	C(24)-C(25)	1.355 (33)
C(13)-C(16)	1.472 (44)	C(23)-C(26)	1.435 (37)
C(16)-C(17)	1.315 (42)	C(26)-C(27)	1.347 (42)
Cl(1)-Pt-Cl(2)	91.6 (3)	N(2)-Pt-Cl(2)	177.9 (6)
N(1)-Pt-Cl(2)	88.7 (6)	Pt-N(1)-C(11)	123.8 (17)
N(2)-Pt-Cl(1)	90.4 (6)	Pt-N(1)-C(15)	121.5 (17)
N(1)-Pt-N(2)	89.3 (8)	Pt-N(2)-C(21)	123.9 (17)
N(1)-Pt-Cl(1)	175.9 (6)	Pt-N(2)-C(25)	123.1 (17)
N(1)-C(11)-C(12)	121.0 (24)	N(2)-C(21)-C(22)	125.3 (25)
C(11)-C(12)-C(13)	122.1 (26)	C(21)-C(22)-C(23)	120.0 (27)
C(12)-C(13)-C(14)	117.0 (24)	C(22)-C(23)-C(24)	116.7 (26)
C(13)-C(14)-C(15)	119.9 (24)	C(23)-C(24)-C(25)	117.9 (26)
C(14)-C(15)-N(1)	125.4 (24)	C(24)-C(25)-N(2)	127.0 (25)
C(15)-N(1)-C(11)	114.3 (21)	C(25)-N(2)-C(21)	113.0 (21)
C(12)-C(13)-C(16)	119.6 (24)	C(22)-C(23)-C(26)	123.1 (28)
C(14)-C(13)-C(16)	123.3 (24)	C(24)-C(23)-C(26)	120.2 (27)
C(13)-C(16)-C(17)	123.6 (28)	C(23)-C(26)-C(27)	126.7 (34)

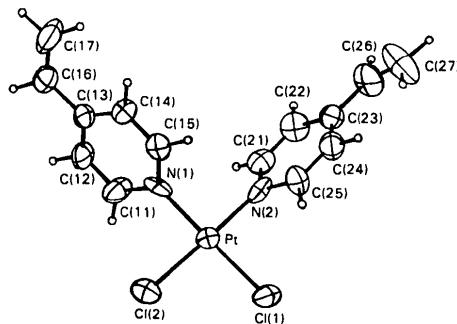


Fig. 1. A view of the title complex, showing the atom numbering.

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters and details of least-squares-plane calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43176 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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 $\text{PtCl}_2(\text{vinylpyridine})_2$ with adjacent molecules held by van der Waals forces.

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

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Abstract. Compound (*A*): $[\text{Zn}(\text{C}_5\text{H}_2\text{N}_2\text{O}_4)(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}$, $M_r = 309.54$, triclinic, $P\bar{1}$, $a = 7.243$ (4), $b = 8.390$ (3), $c = 10.105$ (4) Å, $\alpha = 80.10$ (3), $\beta = 109.23$ (3), $\gamma = 113.69$ (3)°, $V = 530.4$ Å³, $Z = 2$, $D_m = 1.94$ (2), $D_x = 1.938$ g cm⁻³, $\text{Mo K}\alpha$, $\lambda = 0.71073$ Å, $\mu = 24.3$ cm⁻¹, $F(000) = 316$, $T \sim 293$ K, final $R = 0.036$ for 3151 observed unique reflections. Compound (*B*): $[\text{Ni}(\text{C}_5\text{H}_2\text{N}_2\text{O}_4)(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}$, $M_r = 302.86$, triclinic, $P\bar{1}$, $a = 7.240$ (3), $b = 8.298$ (3), $c = 10.076$ (4) Å, $\alpha = 80.11$ (3), $\beta = 109.64$ (3), $\gamma = 114.38$ (3)°, $V = 518.9$ Å³, $Z = 2$, $D_m = 1.93$ (2), $D_x = 1.938$ g cm⁻³, $\text{Mo K}\alpha$, $\lambda = 0.71073$ Å, $\mu = 19.1$ cm⁻¹, $F(000) = 312$, $T \sim 293$ K, final $R = 0.036$ 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;

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

References

- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 KUDUK-JAWORSKA, J. (1985). *Pol. J. Chem.* **59**, 705–712.
 NAVARRO-RANNINGER, M. C., MARTÍNEZ-CARRERA, S. & GARCÍA-BLANCO, S. (1985). *Acta Cryst.* **C41**, 21–22.
 ROCHON, F. D., KONG, P. C. & MELANSON, R. (1980). *Can. J. Chem.* **58**, 97–101.
 Syntex (1976). *XTL/XTLE Structure Determination System*. Syntex Analytical Instruments, Cupertino, California.
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

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, Zgłinska & 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 ($2\theta > 30^\circ$) at 293 ± 1 K. Intensity data [$\sin\theta/\lambda$ max. 0.7078 (*A*), 0.7425 Å⁻¹ (*B*)]

* 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.