Table 1. *Selected geometric parameters (Å, °)*

Ni—N3	2.077 (3)	O5—V1$^{\rm i}$	1.790 (2)
Ni—N6	2.085 (2)	N1—C1	1.340 (4)
Ni—N1	2.086 (2)	N1—C5	1.349 (4)
Ni—N5	2.095 (3)	N2—C10	1.338 (4)
Ni—N2	2.101 (3)	N2—C6	1.349 (4)
Ni—N4	2.112 (2)	C1—C2	1.376 (5)
V1—O1	1.621 (2)	C2—C3	1.367 (5)
V1—O2	1.638 (2)	C3—C4	1.382 (5)
V1—O5$^{\rm i}$	1.790 (2)	C4—C5	1.388 (5)
V1—O6	1.803 (2)	C5—C6	1.474 (4)
V2—O4	1.638 (2)	C6—C7	1.380 (5)
V2—O3	1.641 (3)	C7—C8	1.379 (5)
V2—O5	1.782 (2)	C8—C9	1.375 (5)
V2—O6	1.784 (2)	C9—C10	1.370 (5)
N3—Ni—N6	168.80 (10)	O2—V1—O6	107.40 (12)
N3—Ni—N1	94.37 (10)	O5$^{\rm i}$—V1—O6	111.30 (11)
N6—Ni—N1	95.40 (10)	O4—V2—O3	108.75 (14)
N3—Ni—N5	95.15 (10)	O4—V2—O5	109.73 (12)
N6—Ni—N5	78.53 (10)	O3—V2—O5	109.75 (13)
N1—Ni—N5	95.21 (10)	O4—V2—O6	109.60 (12)
N3—Ni—N2	92.07 (10)	O3—V2—O6	111.43 (13)
N6—Ni—N2	95.27 (10)	O5—V2—O6	107.56 (12)
N1—Ni—N2	78.21 (10)	V2—O5—V1$^{\rm i}$	155.6 (2)
N5—Ni—N2	170.60 (10)	V2—O6—V1	135.64 (14)
N3—Ni—N4	78.74 (10)	C1—N1—C5	118.2 (3)
N6—Ni—N4	92.31 (10)	N1—C1—C2	122.9 (3)
N1—Ni—N4	169.35 (10)	C3—C2—C1	119.1 (3)
N5—Ni—N4	93.51 (10)	C2—C3—C4	119.0 (3)
N2—Ni—N4	93.80 (10)	C3—C4—C5	119.3 (4)
O1—V1—O2	107.92 (15)	N1—C5—C4	121.5 (3)
O1—V1—O5$^{\rm i}$	109.31 (13)	N1—C5—C6	115.8 (3)
O2—V1—O5$^{\rm i}$	109.75 (13)	C4—C5—C6	122.7 (3)
O1—V1—O6	111.07 (14)		

Symmetry code: (i) $-x, 2-y, 1-z$.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL-Plus* (Siemens, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1193). Services for accessing these data are described at the back of the journal.

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Potassium 3-Formyl-2,4-dinitrophenolate Dihydrate

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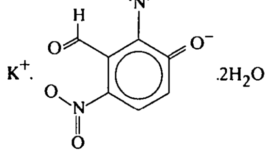
Abstract

The extended conjugation of the phenoxide O atom in the title compound, $K^+.C_7H_3N_2O_6^-.2H_2O$, gives the ring a slight quinonoid character. The substituents deviate significantly from the plane of the ring, the largest deviations being those of the formyl, 2-nitro and 4-nitro groups, which are twisted by 81 (1), 45.06 (15) and 9.08 (12)°, respectively. The structure consists of infinite chains running along the *c* axis. These chains are stacked perpendicular to the shortest axis, *a*, in two alternating layers related by the 2_1 screw axis. The cation is coordinated by six O atoms at distances of 2.750 (2)–2.972 (2) Å. The phenoxide O atom does not belong to the first coordination shell; it is an acceptor with respect to the water molecules in a three-dimensional network of hydrogen bonds.

Comment

The title compound, (I), was synthesized as a precursor for the synthesis of *meso*-aryl-substituted porphyrins, designed to be used in the preparation of metalloporphyrins for oxidation catalysis.



(I)

According to a search of the April 1996 version of the Cambridge Structural Database (Allen *et al.*, 1991), this is the first crystal structure of a 3-formyl-2,4-dinitrophenolate to be reported. Related compounds for which crystal structures have been determined include potassium and ammonium nitrophenolates (Krogh Andersen *et al.*, 1989) and an *o*-nitrophenolate hemihydrate (Richards, 1961; Krogh Andersen & Krogh Andersen, 1975); the structures of a number of nitro- and dinitrophenolates of sodium (Minemoto *et al.*, 1992), barium (Kanters *et al.*, 1984*a*,*b*) and organic cations (But *et al.*, 1987) have also been reported.

In the title compound, the phenolate C—O bond is 0.076 Å shorter than the C_{ar}—OH bond in phenol, although it is significantly longer than a pure C=O bond. The C—C bonds adjacent to the phenolic O atom are lengthened by about 0.03 Å to approach the value of a C_{sp^2}—C(=O)—C_{sp^2} bond and, as a result, the C6—C1—C2 ring angle at the phenolic site is reduced to 114.8 (2)°. In addition, the bond length between the two unsubstituted C atoms of the ring is significantly shorter than the other ring bonds. It should also be remarked that the length of the C—N bond opposite the phenolic group is 0.017 Å shorter than the corresponding bond of the nitro group in the *ortho* position. Similar ring distortions have been found in other *o*-nitrophenolates and were interpreted as evidence of a partial quinonoid character of the ring (Bush & Truter, 1971) and second-order hybridization at the C atoms with neighbouring substituents (Hughes, 1975).

We have performed an *ab initio* calculation at the 6–31G** level for the free anion using the quantum-mechanical package *GAMESS* (Schmidt *et al.*, 1993). The equilibrium geometry corresponding to the minimum energy found by the conjugate gradient method ($\Delta\rho$ at SCF cycle: 10^{-5} bohr^{-3}; maximum gradient: 10^{-4} hartree bohr^{-1}) reproduces the major features of the observed molecular geometry. Bond lengths are in good agreement with experimental values, with the exceptions of C1—O1 [calculated 1.213, observed 1.286 (3) Å] and C4—N2 [calculated 1.407, observed 1.439 (3) Å]. The calculated values for the ring angles C2—C1—C6, C1—C2—C3 and C1—C6—C5 are 113.1, 124.2 and 122.8°, respectively. An analysis of the Mulliken population confirms that some delocalization of the anionic charge occurs.

The benzene ring is planar within 0.02 Å, but the substituents are not coplanar with the benzene ring. The twist angle of the 2-nitro group around the C—N bond is 45.06 (15)° and that of the 4-nitro group is 9.08 (12)°. The dihedral angle between the formyl group and the benzene ring is 81 (1)°. The large twist angles of the formyl and O3—N1—O4 groups can be ascribed to molecular overcrowding at the *ortho*-C2 atom and are reproduced in the *ab initio* quantum calculations for the free anion. In reported structures of 2-nitrophenolates (Kanters *et al.*, 1984*a*,*b*), the twist angle is of the order of 15°, but in our case, the dominant quinonoid character reduces significantly the twist angle of the 4-nitro group compared with that of the 2-nitro group. The phenolic O atom, which is hydrogen bonded with the water molecules (see below), is also significantly displaced out of the benzene ring plane [0.089 (3) Å].

The K$^+$ ion has a coordination polyhedron of six O atoms at distances in the range 2.750 (2)–2.972 (2) Å. The coordination shell includes four water molecules, the O2 atom of the carbonyl group of a phenolate ion and the O5 atom of the 4-nitro group of a neighbouring phenolate ion (Fig. 2). The phenolic O1 atom does not belong to the first coordination shell of the cation: the shortest K$^+\cdots$O1 distance is 4.272 (2) Å. The K$^+\cdots$O distances are comparable to those found in potassium *o*-nitrophenolate hemihydrate (Krogh Andersen & Krogh Andersen, 1975).

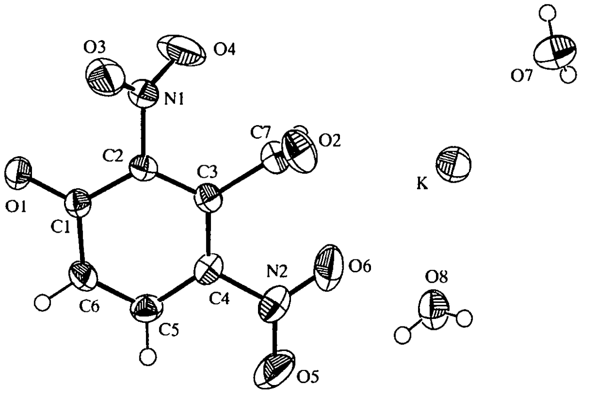


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level; H atoms are represented as spheres of arbitrary radii.

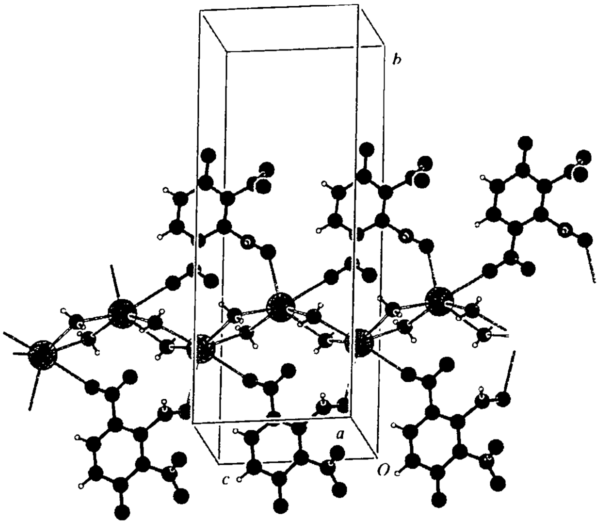


Fig. 2. View of the crystal packing showing the coordination of the K$^+$ ion. For simplicity, only one of the chains running along the *c* axis is shown.

The structure consists of infinite chains running along the *c* axis (Fig. 2). These chains are stacked perpendicular to the shortest axis, *a*, on two alternating layers related by the 2_1 screw axis. The crystal packing is stabilized by an extensive three-dimensional network of hydrogen bonds between the water molecules, the 2-nitro group and the phenolic O atom. One of the water molecules shares one proton between O1 and O3 in a bifurcated hydrogen bond [the sum of the angles around the H atom is 360 (4)°]; the remaining protons of the water molecules are oriented towards the lone pairs of the phenolic O atom.

Experimental

Pure nitric acid (2 ml) was added to a solution of *m*-hydroxybenzaldehyde (2 g, 14.7 mmol) in 10 ml acetic acid. The solution was heated to 353 K for 1 h and then poured into 200 ml of water and neutralized with potassium carbonate. After a few days of slow evaporation, the solution produced a yellow solid that was filtered off and recrystallized first from acetone–water and then from an ethanol–water solution to give 0.880 g (24% yield) of the title compound. ^{1}H NMR (300 MHz, DMSO) δ (p.p.m.): 10.2 (*s*, 1H, CHO), 7.89 (*d*, Ar–H, J = 9.9 Hz), 6.56 (*d*, Ar–H, J = 9.9 Hz). ^{13}C (75 MHz, DMSO) δ (p.p.m.): 191.8, 170.5, 138.4, 135.8, 129.9, 129.0, 126.6. IR (KBr), ν_{max} (cm^{-1}): 3400 (*bb*), 1694 (*m*), 1603 (*s*), 1547 (*s*), 1466 (*s*), 1456 (*s*), 1390 (*m*), 1315 (*s*), 1302 (*s*), 1250 (*s*), 1157 (*m*), 983 (*w*), 839 (*w*), 723 (*w*), 671 (*w*) cm^{-1}. Elemental analysis: $C_7H_7KN_2O_8$ requires N 11.2, H 1.21, C 33.6%; found: N 11.1, H 1.6, C 33.9%.

Crystal data

$K^+.C_7H_3N_2O_6^-.2H_2O$
$M_r = 286.25$
Monoclinic
$P2_1/c$
$a = 7.2897\ (5)$ Å
$b = 19.692\ (3)$ Å
$c = 7.523\ (2)$ Å
$\beta = 92.18\ (2)°$
$V = 1079.2\ (3)$ Å^3
$Z = 4$
$D_x = 1.762$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.29–18.78°$
$\mu = 0.532$ mm^{-1}
$T = 293\ (2)$ K
Truncated pyramid
$0.45 \times 0.25 \times 0.15$ mm
Translucent dark orange

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.80$, $T_{max} = 0.92$
4682 measured reflections
1883 independent reflections

1473 reflections with $I > 2\sigma(I)$
$R_{int} = 0.050$
$\theta_{max} = 25°$
$h = -8 \rightarrow 8$
$k = -23 \rightarrow 23$
$l = -8 \rightarrow 5$
3 standard reflections frequency: 180 min intensity decay: 2.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.089$
$S = 1.075$
1883 reflections
180 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0308P)^2 + 0.4504P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.294$ e Å^{-3}
$\Delta\rho_{min} = -0.252$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C1—O1	1.286 (3)	N1—O3	1.218 (2)
C1—C6	1.423 (3)	N1—O4	1.221 (2)
C1—C2	1.426 (3)	N2—O5	1.218 (3)
C2—C3	1.390 (3)	N2—O6	1.227 (3)
C2—N1	1.456 (3)	K···O5	2.761 (2)
C3—C4	1.393 (3)	K···O7^{i}	2.750 (2)
C3—C7	1.506 (3)	K···O8^{ii}	2.781 (2)
C4—C5	1.393 (3)	K···O8	2.800 (2)
C4—N2	1.439 (3)	K···O7^{iii}	2.954 (2)
C5—C6	1.368 (3)	K···O2^{iv}	2.9722 (19)
C7—O2	1.201 (3)		
C6—C1—C2	114.80 (19)	C5—C4—C3	121.72 (19)
C3—C2—C1	124.16 (18)	C6—C5—C4	119.89 (19)
C2—C3—C4	116.98 (18)	C5—C6—C1	122.33 (19)

Symmetry codes: (i) $2 - x, 1 - y, 2 - z$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $2 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (iv) $x, y, 1 + z$.

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H7*A*···O1^{i}	0.82 (3)	2.20 (3)	3.002 (2)	169 (3)
O7—H7*B*···O1^{ii}	0.77 (3)	2.16 (4)	2.932 (2)	175 (3)
O8—H8*A*···O1^{iii}	0.78 (3)	2.16 (3)	2.934 (3)	172 (3)
O8—H8*B*···O1^{iv}	0.80 (3)	2.18 (4)	2.959 (3)	164 (3)
O8—H8*B*···O3^{iv}	0.80 (3)	2.52 (3)	3.014 (3)	121 (3)

Symmetry codes: (i) $x, 1 + y, z$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iv) $1 - x, -y, 1 - z$.

The title structure was solved by direct methods. The H atoms of the organic moiety were placed at calculated positions and refined as riding. The positions of the H atoms of the water molecules were determined from a difference Fourier synthesis and refined with an isotropic displacement parameter of $1.5U_{eq}$ of the parent O atom. Examination of the crystal structure with *PLATON* (Spek, 1995) showed that there are no additional solvent-accessible voids in the crystal lattice. All calculations were performed on a Pentium 150 MHz PC running LINUX.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP-Plus* (Frenz, 1985). Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1160). Services for accessing these data are described at the back of the journal.

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Two-Dimensional Stacking of Dichloro(dipyridophenazine)platinum(II)

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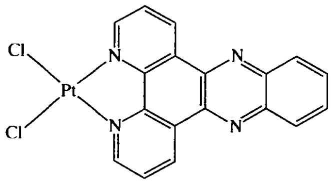
Abstract

A novel platinum(II) complex, dichloro(dipyrido[3,2-*a*:2′,3′-*c*]phenazine-N^4,N^5)platinum(II), $[PtCl_2(C_{18}H_{10}N_4)]$, forms a two-dimensional stacking structure which is constructed with both platinum–platinum and ligand π–π interactions in the crystal.

Comment

Platinum complexes with α-diimines display characteristic emission properties which arise from various intermolecular interactions such as metal–metal and ligand π–π interactions (Houlding & Miskowski, 1991; Kato *et al.*, 1996). They are also of interest as building blocks for new network systems with a view to charge transport or electrical conductivity. We report here a novel platinum(II) complex containing dipyridophenazine (dppz), namely, $[PtCl_2(dppz)]$, (I), which forms a unique two-dimensional stacking structure constructed with platinum–platinum and ligand π–π interactions in the crystal.



(I)

The dppz ligand has been one of the most attractive ligands since $[Ru(bpy)_2(dppz)]^{2+}$ (bpy is 2,2′-bipyridine) was found to be a good luminescence probe for DNA (Friedman *et al.*, 1990). The emission properties of the ruthenium complex are very sensitive to the environment because of the π–π and hydrogen-bonding interactions of dppz (Amouyal *et al.*, 1990; Chambron & Sauvage, 1991; Sabatani *et al.*, 1996). Thus, similar interesting intermolecular interactions are expected for the platinum complexes with square-planar geometry.

The $[PtCl_2(dppz)]$ complex has planar geometry although it does not have any crystallographic symmetry (Fig. 1). Deviations of all atoms in the complex from the mean plane defined by platinum and its four coordination atoms are within 0.1 Å. In the crystal, the platinum complexes are stacked in an antiparallel arrangement, but slipped laterally to make a two-dimensional (2D) layer (Fig. 2). This layer consists of zigzag chains of Pt atoms with alternating Pt···Pt distances [3.4765 (7) and 4.2854 (7) Å] and infinite π-stacks of phenazine moieties [interplanar spacings of 3.44 (1) and 3.45 (1) Å]. The 2D layer seems to be formed as a result of the two competing intermolecular interactions. It was initially obtained using dppz with a π-system extended toward the opposite side of the coordinating N atoms. Furthermore, it is noteworthy that weak C—H···N hydrogen bonds exist between the phenazine sites of the adjacent 2D layers, forming channels between the layers [N4···C16^{i} 3.48 (1), N4···H9^{i} 2.90 Å and N4···H9^{i}—