4,4'-(Azinodimethylene)dipyridinium chloranilate dichloromethane disolvate

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The dichloromethane disolvate of 4,4'-(azinodimethylene)-dipyridinium chloranilate, $C_{12}H_{12}N_4^{2+} \cdot C_6Cl_2O_4^{2-} \cdot 2CH_2Cl_2$, consists of one-dimensional hydrogen-bonded molecular tapes that propagate along the $[1\bar{2}0]$ direction. Both cations and anions lie across centres of inversion. The molecular tapes are planar but do not stack in the expected segregated manner, instead having chloranilate anions sandwiched between azine groups.

Comment

The metal binding pyridyl group and central chromophore of 4-pyridinealdazine give it the properties needed for use in surface enhanced resonance Raman scattering, and as such it has been used in our laboratories for the detection of explosive traces (McHugh *et al.*, 2002) and to probe the nature of species bound to the surface of silver nanoparticles (Kennedy *et al.*, 2003). These same features also make the azine a candidate for reaction with chloranilic acid. Work by Tomura and co-workers (Zaman *et al.*, 1999, 2000, 2001; Akhtaruzzaman *et al.*, 2002) suggests that a simple acid–base reaction should occur, giving a strongly hydrogen-bonded structure. We wished to determine what effect, if any, this behaviour would have on the nature of the chromophore.

Crystals grown using layering methods were shown to be the dichloromethane disolvate of a 1:1 complex, *viz.* 4,4'-(azinodimethylene)dipyridinium chloranilate, (I), of the starting materials. Two different crystal morphologies, namely red needles and orange plates, were observed; these were found to give identical unit-cell parameters and so were attributed to the same phase. Both the cations and the anions lie on inversion centres (Fig. 1). The bond lengths (Table 1) of the chloranilate ring show that the C—C bonds between the O substituents are almost entirely single in character, whilst the C8—C9 bond has a high proportion of double-bond character, thus supporting the quinone formulation drawn. The

geometry of the azine backbone does not seem to be altered by protonation of the pyridyl rings, being essentially identical to the geometry observed in the neutral molecule (Ciurtin *et al.*, 2001) and in Ag^I complexes (Kennedy *et al.*, 2003). The only difference is a marked widening of the ring C2—N2—C6 angle from 116.3 to 122.2 (3)° upon protonation, thus leaving the protonated azine geometrically identical to the state found in its diperchlorate salt (Chen *et al.*, 1997).

(I)
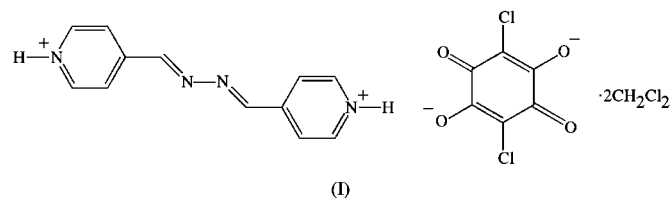
The cations and anions are linked by asymmetric bifurcated hydrogen bonds of the $R_1^2(5)$ type into one-dimensional molecular tapes running along the $[1\bar{2}0]$ direction. This structure agrees with the predictions of earlier work on such chloranilate complexes, although with an N2···O2 distance of 2.584 (4) Å (Table 2) the dominant leg of the hydrogen bond is shorter than those seen previously (Zaman *et al.*, 2001). We note a small electron-density peak, of 0.29 e Å^{-3}, 1.05 Å from atom O2, suggesting that atom H2N, the H atom involved in this bond, may not exhibit full occupancy of the site bonded to atom N2. Indeed, an alternative model with full isotropic refinement of the H atoms moves atom H2N to a position intermediate between atoms N2 and O2, and gives it a U_{iso} value 3–4 times larger than those of the other H atoms. This fact may indicate that this strong interaction is based on an equilibrium between N—H···O and N···H—O interactions. The O1—C7 and O2—C8 distances [1.243 (4) and 1.274 (4) Å] indicate that, as expected, the hydrogen bonding is dominated by the group with the most single-bond character. Both the constituents of the molecular tape are planar, and there is an angle of only 5.4 (3)° between the chloranilate and pyridyl ring planes. Zaman *et al.* (2001) state that such planar tapes should give segregated stacks of donor and acceptor ions. However, in
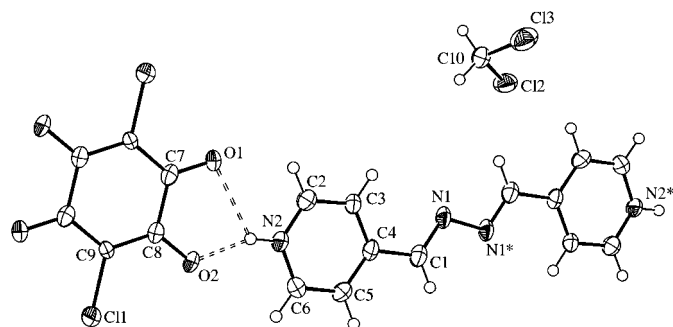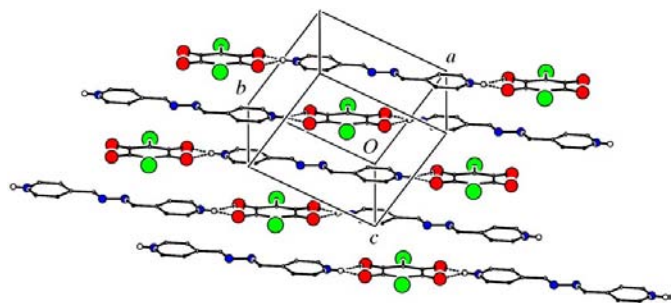

Figure 1
The molecular structure of (I), with 50% probability displacement ellipsoids. Atoms marked with an asterisk (*) are at the symmetry position $(-x, 1-y, 1-z)$.

organic compounds

Figure 2
A view of the crystal packing of (I), showing the alternating donor and acceptor groups within each stack. Solvent molecules have been omitted for clarity.

this case, it is clear that (I) stacks with alternate donor and acceptor groups (Fig. 2). As all previous work was based on bipyridyls with carbon backbones, this behaviour may be due to the heteroatomic nature of the azine link between the pyridyl rings. However, no significant azine-to-chloranilate intermolecular interactions were found, and only the Cl atoms form contacts [$Cl1 \cdots Cl1 = 3.280\ (2)$ Å] that are significantly shorter than the sum of the relevant van der Waals radii (Bondi, 1964).

Experimental

The title compound was isolated in 80% yield by addition of equimolar solutions of chloranilic acid in acetone and 4-pyridinealdazine in dichloromethane. After stirring for 30 min, the product was isolated as a powder by filtration. Suitable crystals were grown over a period of 2 d by careful layering of the acetone solution onto the dichloromethane solution. [Note: the potential danger of acetone/chlorocarbon solvent mixtures was minimized by keeping reagent quantities to a minimum and by use of a suitable fume-hood.]

Crystal data

$C_{12}H_{12}N_4^{2+} \cdot C_6Cl_2O_4^{2-} \cdot 2CH_2Cl_2$	$Z = 1$
$M_r = 589.07$	$D_x = 1.641$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.6066\ (9)$ Å	Cell parameters from 2303
$b = 8.7846\ (9)$ Å	reflections
$c = 9.3316\ (11)$ Å	$\theta = 2.9–27.0°$
$\alpha = 99.918\ (4)°$	$\mu = 0.76$ mm^{-1}
$\beta = 95.556\ (4)°$	$T = 123\ (2)$ K
$\gamma = 101.534\ (5)°$	Plate fragment, dark orange
$V = 596.23\ (12)$ Å^3	$0.25 \times 0.12 \times 0.05$ mm

Data collection

Nonius KappaCCD area-detector diffractometer	$R_{int} = 0.091$
ω and φ scans	$\theta_{max} = 27.7°$
8528 measured reflections	$h = -9 \rightarrow 9$
2472 independent reflections	$k = -11 \rightarrow 11$
1336 reflections with $I > 2\sigma(I)$	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.058$	$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2]$
$wR(F^2) = 0.151$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.98$	$(\Delta/\sigma)_{max} = 0.001$
2472 reflections	$\Delta\rho_{max} = 0.43$ e Å^{-3}
154 parameters	$\Delta\rho_{min} = -0.49$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—C9	1.745 (4)	N1—N1^i	1.411 (6)
O1—C7	1.243 (4)	C7—C9^{ii}	1.424 (5)
O2—C8	1.274 (4)	C7—C8	1.524 (6)
N1—C1	1.278 (5)	C8—C9	1.368 (5)
C1—N1—N1^i	110.6 (4)	O2—C8—C9	124.2 (4)
N1—C1—C4	118.3 (4)	O2—C8—C7	116.4 (3)
O1—C7—C9^{ii}	124.7 (4)	C9—C8—C7	119.4 (3)
O1—C7—C8	118.4 (3)	C8—C9—C7^{ii}	123.7 (4)
C9^{ii}—C7—C8	116.9 (4)		
N1^i—N1—C1—C4	−179.6 (4)	N1—C1—C4—C3	−1.8 (6)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1-x, -1-y, 1-z$.

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2—H2N$\cdots$O1	0.88	2.39	2.987 (4)	126
N2—H2N$\cdots$O2	0.88	1.76	2.584 (4)	155

The sample consisted largely of non-singular fragments. The crystal used was a fragment cut from a larger non-single crystal, but still many of the peaks were badly split. Although most of the frames could be processed successfully, inclusion of one of the runs degraded the quality of the data set. This run has therefore been omitted, leading to a slightly low completeness of 0.973. All H atoms were located by difference synthesis but were included in the final model in calculated positions and in riding modes [$U_{iso}(H) = 1.2U_{eq}$(parent), N—H = 0.88 Å, methylene C—H = 0.99 Å and other C—H = 0.95 Å].

Data collection: *DENZO* (Otwinowski & Minor, 1997); *COLLECT* (Hooft, 1988); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); 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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