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Key indicators

Single-crystal X-ray study
 $T = 292$ K
Mean $\sigma(\text{C}-\text{C}) = 0.008$ Å
 R factor = 0.065
 wR factor = 0.196
Data-to-parameter ratio = 9.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.A cocrystal of 3-nitrophenylanilinium
perchlorate and 3-nitroaniline

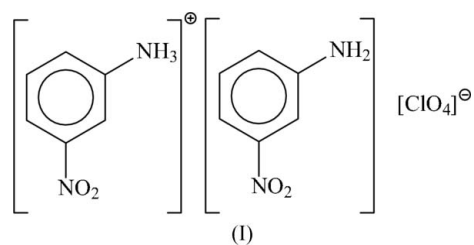
3-Nitroanilinium perchlorate crystallizes with a molecule of 3-nitroaniline to give the title compound, $\text{C}_6\text{H}_7\text{N}_2\text{O}_2^+ \cdot \text{ClO}_4^- \cdot \text{C}_6\text{H}_6\text{N}_2\text{O}_2$; all atoms except one O atom of the perchlorate ion and two H atoms bonded to nitrogen lie on a mirror plane. Hydrogen bonds link the cation, anion and neutral molecule into a chain that runs along the c axis of the orthorhombic unit cell.

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Comment

The Schiff base that is derived by condensing acetylacetone and a substituted aniline rearranges itself upon being deprotonated in order to chelate to copper (Atakol *et al.*, 1997; Barclay & Hoskins, 1965; Elmali *et al.*, 1997; Tahir *et al.*, 1996). In our hands, in the reaction of the 3-nitro substituted ligand with copper perchlorate, the ligand is cleaved (probably to starting reactants). The 3-nitroaniline portion separates from solution in the protonated form, as well as a neutral molecule, to give the title compound, (I) (Fig. 1). The cation, molecule and anion are linked by hydrogen bonds (Table 1 and Fig. 2) into a chain that runs along the c axis of the orthorhombic unit cell. The cation and the molecule are located on alternate sides of the ribbon. The crystal structure of anilinium perchlorate has been reported; this salt exists as a hydrogen-bonded compound (Paixão *et al.*, 1997), but the hydrogen bonds are much weaker than those in the present compound.



Experimental

Acetylacetone (3 ml, 0.03 mol), 3-nitroaniline (4.14 g, 0.03 mol) and a catalytic amount of *p*-toluenesulfonic acid were dissolved in toluene (30 ml). The mixture was refluxed for 6 h and the water was separated azeotropically in a Dean–Stark apparatus. The solvent was removed and the product purified by recrystallization from hexane to yield 4-(3-nitrophenylamino)-3-penten-2-one in 80% yield. To a chloroform (5 ml) solution of the ligand (50 mg, 0.23 mmol) was added triethylamine (0.32 ml, 0.23 mmol) and copper perchlorate (60 mg, 0.23 mmol) dissolved in ethanol (25 ml). The resulting brown mixture was filtered and the solution set aside for several days to allow for the formation of crystals. Copper was not incorporated into the crystal-

line product. CH&N elemental analysis calculated for $C_{12}H_{13}ClN_4O_8$:
C 38.26, H 3.48, N 14.88%; found: C 38.60, H 3.29, N 14.63%.

Crystal data

$C_6H_7N_2O_2^+ \cdot ClO_4^- \cdot C_6H_6N_2O_2$
 $M_r = 376.71$
Orthorhombic, *Pbcm*
 $a = 7.9181$ (3) Å
 $b = 30.848$ (2) Å
 $c = 6.3894$ (4) Å
 $V = 1560.7$ (1) Å³

$Z = 4$
 $D_x = 1.603$ Mg m⁻³
Mo $K\alpha$ radiation
 $\mu = 0.30$ mm⁻¹
 $T = 292$ (2) K
Block, colorless
0.20 × 0.10 × 0.10 mm

Data collection

Bruker APEX area-detector
diffractometer
 φ and ω scans
Absorption correction: None
14008 measured reflections

1512 independent reflections
1402 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.031$
 $\theta_{max} = 25.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.065$
 $wR(F^2) = 0.196$
 $S = 1.05$
1512 reflections
159 parameters
H atoms treated by a mixture of
independent and constrained
refinement

$w = 1/[\sigma^2(F_o^2) + (0.1029P)^2 + 3.8634P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.34$ e Å⁻³
 $\Delta\rho_{min} = -0.80$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1n2 \cdots O1^{ii}$	0.85 (1)	1.90 (1)	2.748 (6)	177 (6)
$N1-H1n1 \cdots O2^i$	0.85 (1)	1.91 (1)	2.760 (4)	174 (4)
$N3-H3n1 \cdots O2$	0.85 (1)	2.20 (2)	2.929 (5)	144 (4)

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

The three ammonium and two amino H atoms were located in a difference Fourier map and were refined with a distance restraint of $N-H = 0.85$ (1) Å; their displacement parameters were freely refined. All other H atoms were placed in calculated positions [$C-H = 0.93$ Å and $U_{iso}(H) = 1.2U_{eq}(C)$], and were included in the refinement in the riding-model approximation.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *SHELXL97*.

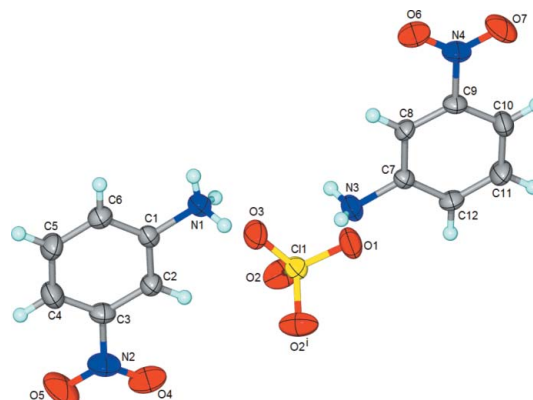


Figure 1

Structure of the title compound. Displacement ellipsoids are plotted at the 50% probability level and H atoms as spheres of arbitrary radii. [Symmetry code: (i) $x, y, \frac{1}{2} - z$.]

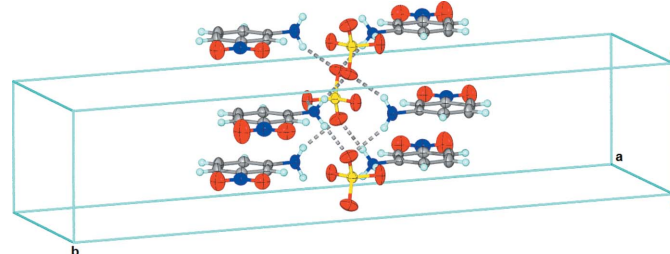


Figure 2

Hydrogen-bonded (dashed lines) chain structure.

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