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Hexamethylenetetraminium 2,4,6-trinitrophenolate

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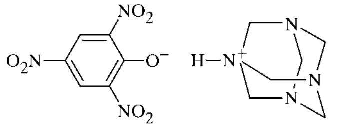
In the title complex, the 1:1 ionic adduct of hexamethylenetetraminium and 2,4,6-trinitrophenolate, $C_6H_{13}N_4^+\cdot C_6H_2N_3O_7^-$, the cation acts as a donor for bifurcated hydrogen bonds to the O atoms of the phenolate and one of the nitro groups of the 2,4,6-trinitrophenolate anion. The crystal structure is built from sheets of cations and anions, and is stabilized by intermolecular C—H···O and C—H···π interactions.

Comment

The crystal structures of the adducts of hexamethylenetetramine (HMT) and mono-, di- or triphenol derivatives have been investigated intensively (Jordan & Mak, 1970; Mak *et al.*, 1977, 1978; Mahmoud & Wallwork, 1979; Coupar, Glidewell & Ferguson, 1997; Coupar, Ferguson *et al.*, 1997; Ng *et al.*, 2001; Usman *et al.*, 2001). Although HMT usually acts as an acceptor of up to three O—H···N hydrogen bonds or partially acts as a hydrogen bond donor with 4-nitrophenol, we have shown recently that HMT can also act solely as an N—H···O hydrogen donor in the presence of 2,4-dinitrophenol (Usman *et al.*, 2001). In this HMT–2,4-dinitrophenol complex, the phenolic H atom is transferred to HMT. This H-atom transfer process occurs because 2,4-dinitrophenol is a stronger acid than the other phenols investigated. This unusual behaviour of HMT in the solid state is of interest, and led us to the title adduct, (I), where 2,4,6-trinitrophenol (TNP) also acts as a stronger acid.

In (I), the TNP also transfers an H atom from the hydroxy group to the HMT moiety to form the 2,4,6-trinitrophenolate anion (TNP$^-$), making HMT positively charged.

The bond lengths and angles (Table 1) within the hexamethylenetetraminium cation (HMT$^+$) are comparable with those of HMT$^+$ in the polymorphs of hexamethylenetetraminium–2,4-dinitrophenolate (Usman *et al.*, 2001), while those within the TNP$^-$ anion are comparable with those of TNP$^-$ in potassium and ammonium 2,4,6-trinitrophenolate (Maartmann-Moe, 1969). For instance, the mean N—O [1.224 (5) Å] and the C—O bond length in the title complex agree with the mean N—C and C—O bond lengths in the two 2,4,6-trinitrophenolate derivatives reported by Maartmann-Moe (1969) [N—C 1.224 (6) Å and C—O 1.241 (7) Å].



(I)

In the HMT$^+$ cation, the N—C bond distances around the N4 atom are elongated due to the positive charge localized on the protonated N4 atom. The N4—C7, N4—C8 and N4—C9 distances [mean value of 1.518 (2) Å] are equivalent to the typical N—C single-bond length in the trimethylammonium ion (Allen *et al.*, 1987). The protonated N4 atom also slightly affects the π-electron distribution in the surrounding atoms, which can be seen in the shortening by about 0.03 Å of the N5—C7, N6—C8 and N7—C9 distances compared with the other two N5—C, N6—C and N7—C bonds.

In the title adduct, the TNP$^-$ anion is nearly planar, with the nitro groups slightly twisted about their C—N bonds so that the angles between the aromatic ring plane and those of the CNO_2 groupings containing N1, N2 and N3 are 11.06 (1), 7.96 (9) and 5.46 (10)°, respectively. The nitro O2–O7 atoms deviate from the aromatic ring plane by 0.287 (2), −0.114 (2), −0.307 (1), −0.062 (2), 0.175 (2) and −0.017 (2) Å, respectively. For the HMT$^+$ cation, all of the six-membered NCNCNC rings adopt a chair conformation, as shown by their puckering parameters (Cremer & Pople, 1975), which are available from the IUCr archives.

The crystal structure of the title adduct is built from sheets of HMT$^+$ cations and separate sheets of TNP$^-$ anions stacked alternately along the *a* axis. The HMT$^+$ cation acts as an N—H···O hydrogen-bond donor and forms bifurcated interionic hydrogen bonds with both the phenolate-O atom and a nitro-O atom of the same adjacent TNP$^-$ anion (Table 2). These interactions link the HMT$^+$ and TNP$^-$ ions into ion pairs. Interionic C12—H12*A*···O7 and C12—H12*B*···O4 inter-

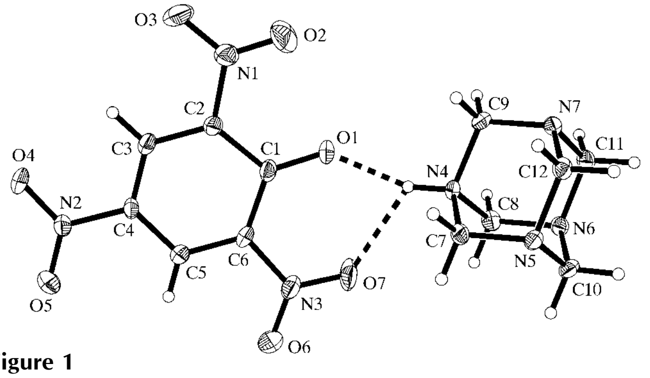


Figure 1
The structure of the title adduct showing 50% probability displacement ellipsoids and the atom-numbering scheme.

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actions connect the ion pairs into infinite two-dimensional networks which lie perpendicular to the *c* axis (Fig. 2). An interionic C5—H5···π interaction involving the aromatic ring centroid (*Cg*) of the TNP^- anion was also observed (Table 2).

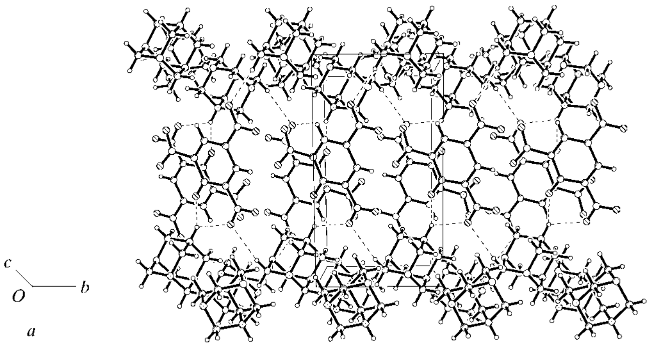

Figure 2
Packing diagram of the title adduct viewed down the *c* axis. The dashed lines denote the interionic hydrogen-bond interactions.

Experimental

Complex (I) was prepared by mixing thoroughly 1.40 g (10 mmol) of hexamethylenetetramine and 2.29 g (10 mmol) of 2,4,6-trinitrophenol, and then dissolving in 50 ml of acetone with a few drops of water. The mixture was warmed until a clear solution was obtained. The solution was filtered and left to evaporate slowly in air. Yellow single crystals were obtained from the solution after a few days.

Crystal data

$C_6H_{13}N_4^+\cdot C_6H_2N_3O_7^-$
$M_r = 369.31$
Monoclinic, $P2_1/c$
$a = 12.4995\ (2)$ Å
$b = 6.6344\ (1)$ Å
$c = 18.6203\ (2)$ Å
$\beta = 107.022\ (1)^\circ$
$V = 1476.48\ (4)$ Å^3
$Z = 4$
$D_x = 1.661$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6652 reflections
$\theta = 3.2$–28.3°
$\mu = 0.14$ mm^{-1}
$T = 183\ (2)$ K
Block, yellow
0.40 × 0.40 × 0.32 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.947$, $T_{\max} = 0.957$
8504 measured reflections
3575 independent reflections
2697 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.069$
$\theta_{\max} = 28.3^\circ$
$h = -16 \rightarrow 16$
$k = -8 \rightarrow 7$
$l = -24 \rightarrow 16$

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.2456 (19)	N5—C7	1.4488 (19)
O2—N1	1.2037 (19)	N5—C10	1.4737 (19)
O3—N1	1.221 (2)	N5—C12	1.474 (2)
O4—N2	1.2393 (18)	N6—C8	1.446 (2)
O5—N2	1.2258 (19)	N6—C11	1.4719 (19)
O6—N3	1.226 (2)	N6—C10	1.472 (2)
O7—N3	1.2262 (18)	N7—C9	1.4431 (19)
N4—C8	1.517 (2)	N7—C11	1.4733 (19)
N4—C9	1.5181 (19)	N7—C12	1.474 (2)
N4—C7	1.519 (2)		
O6—N3—O7	121.20 (15)	O2—N1—O3	121.94 (16)
O5—N2—O4	122.60 (14)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H14N···O1	0.94 (2)	1.81 (3)	2.666 (2)	152 (2)
N4—H14N···O7	0.94 (2)	2.26 (2)	2.865 (2)	122 (2)
C12—H12*A*···O7$^{\rm i}$	0.97	2.49	3.362 (2)	149
C12—H12*B*···O4$^{\rm ii}$	0.97	2.41	3.364 (2)	167
C5—H5*A*···*Cg*$^{\rm iii}$	0.93	3.30	4.07	142

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.154$
$S = 0.95$
3575 reflections
240 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0807P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.43$ e Å^{-3}
$\Delta\rho_{\min} = -0.43$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.033 (4)

The H14N atom was located in a difference Fourier map and was refined freely as an isotropic atom. After checking for H atoms in the difference map, the positions of all remaining H atoms were geometrically idealized and allowed to ride on their parent atoms with C—H distances in the range 0.93–0.97 Å and fixed displacement parameters defined by $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL, PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1125). Services for accessing these data are described at the back of the journal.

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