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Crystal structure of melaminium dipicrylaminate hydrate, $[C_3N_3H(NH_2)_3][N\{C_6H_2(NO_2)_3\}_2] \cdot H_2O$

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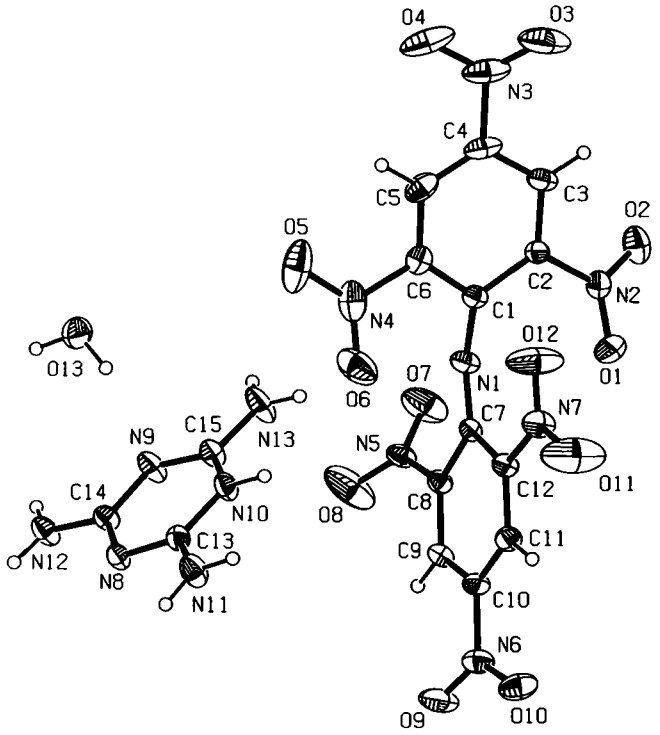

Abstract

$C_{15}H_{13}N_{13}O_{13}$, monoclinic, $P12_1/n1$ (no. 14), a = 11.499(1) Å, b = 9.654(1) Å, c = 20.372(2) Å, β = 90.820(2)°, V = 2261.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.077, $wR_{ref}(F^2)$ = 0.228, T = 291 K.

Source of material

Melamine (0.042 g, 0.5 mmol), 2,4,6,2′,4′,6′-hexanitrodiphenylamine (0.22 g, 0.5 mmol), and NaOH (0.02 g, 0.5 mmol) were dissolved in an aqueous solution (12 mL). The solution was stirred at 353 K for 3 hours, then cooled down to room temperature. After evaporated in air for three days, red crystals of the title compound were obtained.

Discussion

The design and synthesis of supramolecular polymeric networks, especially those constructed by hydrogen bonding and intermolecular weak interactions have been a field of rapid growth due to their special physical properties and potential application in functional materials. The melamine system is very interesting, because (i) it has three nitrogen atoms at the melamine ring, in which one of them may be protonated easily and its amidocyano groups are easy to construct interesting high-dimensional structures, and (ii) it can act not only as hydrogen-bond donor but also as hydrogen-bond acceptor, depending upon the numbers of amidocyanogen groups [1-5]. At the same time, the 2,4,6,2′,4′,6′-hexanitrodiphenylamine can present profuse oxygen atoms, which are able to accept H atoms to form hydrogen bonds [6]. Taking into account of these, we report the molecular assemblies of melamine and 2,4,6,2′,4′,6′-hexanitrodiphenylamine in order to understand the physical-chemical character of the compound in future.

The structure of the title compound comprises a melamine cation, a 2,4,6,2′,4′,6′-hexanitrodiphenylamine anion and a water molecule. The imine group of 2,4,6,2′,4′,6′-hexanitrodiphenylamine is deprotonated and a melamine ring accepts the proton to produce the melaminium cation. Hydrogen bonds play an important role in the structure. There are several kinds of hydrogen bonds in the structure which are listed as below: (a) hydrogen bonds between water molecules and melamine nitrogen atoms with an O(–H)···N distance of 3.025 Å; (b) hydrogen bonds between amido groups of melamine and water molecules with N(–H)···O distances of 2.942 Å and 3.042 Å; (c) hydrogen bonds between water molecules and 2,4,6,2′,4′,6′-hexanitrodiphenylamine oxygen atoms with O(–H)···O distances of 2.905 Å and 3.075 Å; (d) hydrogen bonds between amido groups of melamine and oxygen atoms of 2,4,6,2′,4′,6′-hexanitrodiphenylamine with N(–H)···O distances of 3.302 Å, 3.077 Å, 3.314 Å, 3.255 Å, 3.099 Å, 3.231 Å, 3.188 Å, 2.905 Å, 2.836 Å and 2.994 Å, respectively, (e) hydrogen bonds both of the melamine molecules with N(–H)···N distance of 3.045 Å. Then, an extended three-dimensional network with hydrogen bonds is formed, which contributes to the stability of the crystal structure.

Table 1. Data collection and handling.

Crystal:	red block, size 0.11 × 0.18 × 0.34 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.52 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	19212, 5202
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3738
$N(param)_{refined}$:	370
Programs:	SHELXS-97 [7], SHELXL-97 [8], SHELXTL [9]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(10)	4e	0.6895	0.5338	0.0339	0.050
H(11A)	4e	0.7695	0.8236	–0.0372	0.066
H(11B)	4e	0.8037	0.6777	–0.0231	0.066
H(12A)	4e	0.4076	0.9688	0.0306	0.054
H(12B)	4e	0.3325	0.8706	0.0672	0.054

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(13A)	4e	0.4612	0.4342	0.1186	0.075
H(13B)	4e	0.5781	0.3900	0.0959	0.075
H(3)	4e	0.4534	−0.2512	0.3369	0.051
H(5)	4e	0.3425	−0.0279	0.1816	0.059

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(9)	4e	0.5937	0.6095	0.4223	0.043
H(11)	4e	0.8486	0.4036	0.3314	0.044
H(1W)	4e	0.1701	0.6346	0.0496	0.069
H(2W)	4e	0.2871	0.5789	0.0610	0.061

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4e	0.6171(3)	0.0260(4)	0.4231(2)	0.091(2)	0.063(2)	0.082(2)	−0.017(2)	−0.050(2)	0.005(2)
O(2)	4e	0.5123(3)	−0.1521(3)	0.4446(2)	0.071(2)	0.062(2)	0.057(2)	0.013(2)	0.001(2)	0.021(2)
O(3)	4e	0.3758(4)	−0.3910(4)	0.2438(3)	0.077(3)	0.059(2)	0.177(5)	−0.020(2)	0.022(3)	−0.056(3)
O(4)	4e	0.2767(3)	−0.2650(5)	0.1758(2)	0.071(2)	0.137(4)	0.069(2)	−0.052(2)	0.013(2)	−0.054(2)
O(5)	4e	0.3406(3)	0.2209(5)	0.1706(2)	0.071(2)	0.157(4)	0.065(2)	0.030(2)	−0.001(2)	0.045(2)
O(6)	4e	0.4844(4)	0.3078(4)	0.2252(2)	0.146(4)	0.053(2)	0.063(2)	−0.012(2)	0.006(2)	0.015(2)
O(7)	4e	0.3793(3)	0.3406(4)	0.4366(2)	0.069(2)	0.055(2)	0.142(3)	−0.010(2)	0.054(2)	0.000(2)
O(8)	4e	0.3866(4)	0.5476(4)	0.4133(3)	0.080(3)	0.051(2)	0.239(6)	0.017(2)	0.080(3)	0.007(3)
O(9)	4e	0.7716(3)	0.7469(3)	0.4113(2)	0.062(2)	0.040(2)	0.104(3)	−0.017(1)	0.008(2)	−0.016(2)
O(10)	4e	0.9160(2)	0.6201(3)	0.3804(2)	0.040(2)	0.071(2)	0.074(2)	−0.022(1)	0.009(1)	−0.009(2)
O(11)	4e	0.8494(4)	0.1873(5)	0.2843(3)	0.068(2)	0.118(4)	0.245(6)	−0.018(2)	0.066(3)	−0.096(4)
O(12)	4e	0.6911(3)	0.0950(4)	0.2759(2)	0.058(2)	0.087(3)	0.160(4)	−0.025(2)	0.046(2)	−0.079(3)
O(13)	4e	0.2134(2)	0.5611(3)	0.0515(2)	0.049(2)	0.055(2)	0.071(2)	0.009(1)	−0.005(1)	−0.007(1)
N(1)	4e	0.5005(2)	0.2021(3)	0.3463(2)	0.038(2)	0.030(1)	0.052(2)	−0.004(1)	0.009(1)	−0.006(1)
N(2)	4e	0.5427(3)	−0.0575(3)	0.4082(2)	0.049(2)	0.042(2)	0.048(2)	0.005(1)	−0.010(1)	0.003(1)
N(3)	4e	0.3467(3)	−0.2816(5)	0.2229(2)	0.052(2)	0.076(3)	0.088(3)	−0.027(2)	0.027(2)	−0.051(2)
N(4)	4e	0.4158(3)	0.2153(5)	0.2130(2)	0.062(2)	0.078(3)	0.038(2)	0.023(2)	0.013(2)	0.014(2)
N(5)	4e	0.4298(2)	0.4366(3)	0.4136(2)	0.037(2)	0.029(1)	0.054(2)	−0.002(1)	0.013(1)	−0.005(1)
N(6)	4e	0.8121(3)	0.6361(3)	0.3908(2)	0.049(2)	0.042(2)	0.051(2)	−0.015(1)	0.003(1)	−0.000(1)
N(7)	4e	0.7473(3)	0.1871(3)	0.2946(2)	0.036(2)	0.044(2)	0.064(2)	−0.000(1)	0.015(1)	−0.012(2)
N(8)	4e	0.5791(2)	0.8271(3)	0.0153(1)	0.035(1)	0.029(1)	0.045(2)	0.003(1)	0.006(1)	0.006(1)
N(9)	4e	0.4572(3)	0.6705(3)	0.0743(2)	0.048(2)	0.033(2)	0.062(2)	0.009(1)	0.022(2)	0.013(1)
N(10)	4e	0.6383(3)	0.5981(3)	0.0377(2)	0.037(2)	0.031(1)	0.058(2)	0.009(1)	0.006(1)	0.008(1)
N(11)	4e	0.7544(3)	0.7443(4)	−0.0202(2)	0.037(2)	0.046(2)	0.083(2)	0.009(1)	0.016(2)	0.017(2)
N(12)	4e	0.3970(3)	0.8888(3)	0.0481(2)	0.041(2)	0.031(1)	0.063(2)	0.006(1)	0.018(1)	0.008(1)
N(13)	4e	0.5245(3)	0.4520(3)	0.0983(2)	0.068(2)	0.037(2)	0.083(3)	0.011(2)	0.024(2)	0.027(2)
C(1)	4e	0.4801(3)	0.0860(3)	0.3132(2)	0.026(1)	0.030(2)	0.039(2)	−0.001(1)	0.007(1)	−0.002(1)
C(2)	4e	0.4878(3)	−0.0470(3)	0.3436(2)	0.031(2)	0.030(2)	0.040(2)	−0.001(1)	−0.001(1)	−0.001(1)
C(3)	4e	0.4463(3)	−0.1665(4)	0.3155(2)	0.038(2)	0.031(2)	0.061(2)	−0.005(1)	0.007(2)	−0.009(2)
C(4)	4e	0.3929(3)	−0.1571(4)	0.2537(2)	0.034(2)	0.056(2)	0.059(2)	−0.015(2)	0.011(2)	−0.030(2)
C(5)	4e	0.3809(3)	−0.0329(5)	0.2221(2)	0.036(2)	0.073(3)	0.039(2)	−0.005(2)	0.002(1)	−0.015(2)
C(6)	4e	0.4260(3)	0.0839(4)	0.2504(2)	0.035(2)	0.049(2)	0.036(2)	0.003(2)	0.004(1)	−0.000(2)
C(7)	4e	0.5784(3)	0.2961(3)	0.3543(2)	0.032(2)	0.026(1)	0.033(1)	0.001(1)	0.003(1)	0.002(1)
C(8)	4e	0.5476(3)	0.4214(3)	0.3899(2)	0.033(2)	0.029(2)	0.038(2)	−0.001(1)	0.006(1)	0.001(1)
C(9)	4e	0.6202(3)	0.5307(3)	0.4009(2)	0.042(2)	0.025(1)	0.040(2)	−0.003(1)	0.004(1)	0.001(1)
C(10)	4e	0.7339(3)	0.5227(3)	0.3798(2)	0.036(2)	0.032(2)	0.043(2)	−0.010(1)	0.002(1)	0.002(1)
C(11)	4e	0.7722(3)	0.4076(3)	0.3456(2)	0.031(2)	0.037(2)	0.042(2)	−0.003(1)	0.004(1)	0.002(1)
C(12)	4e	0.6980(3)	0.2997(3)	0.3327(2)	0.032(2)	0.033(2)	0.038(2)	0.000(1)	0.007(1)	−0.002(1)
C(13)	4e	0.6559(3)	0.7249(3)	0.0104(2)	0.033(2)	0.034(2)	0.045(2)	0.003(1)	−0.001(1)	0.003(1)
C(14)	4e	0.4796(3)	0.7939(3)	0.0457(2)	0.039(2)	0.030(2)	0.040(2)	0.002(1)	0.008(1)	0.000(1)
C(15)	4e	0.5397(3)	0.5748(3)	0.0707(2)	0.045(2)	0.032(2)	0.045(2)	0.006(1)	0.006(2)	0.008(1)

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