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A proton-transfer compound: 1,10-phenanthrolinium–2,4,5-tricarboxybenzoate–2,5-dicarboxybenzene-1,4-dicarboxylate (4/2/1)

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.049
wR factor = 0.108
Data-to-parameter ratio = 15.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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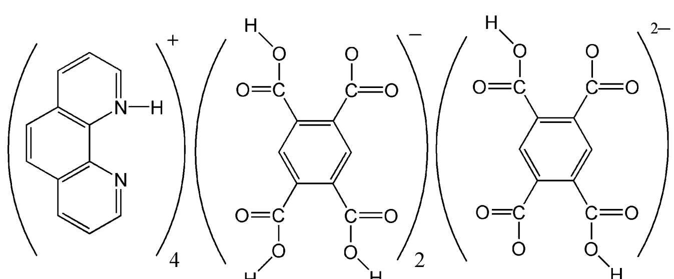
The title compound, $4C_{12}H_9N_2^+\cdot 2C_{10}H_5O_8^-\cdot C_{10}H_4O_8^{2-}$, contains singly and doubly deprotonated tetracarboxylic acids and the protonated form of 1,10-phenanthroline; the dianion is centrosymmetric. The crystal structure is stabilized by strong intermolecular O—H···O and N—H···N hydrogen bonds, linking the ions to form a three-dimensional network.

Comment

Recently, there has been considerable interest in proton-transfer systems and their structures. 1,10-Phenanthroline is a well known *N*-heterocyclic chelating ligand with a rigid planar structure. The metal-chelating properties of 1,10-phenanthroline have been widely utilized in many aspects of coordination chemistry (Bretonniére *et al.*, 2000), including its recent application in the development of biomimetic models of metalloenzymes (Bijloo *et al.*, 1990) and in the preparation of supramolecules (Weidmann *et al.*, 1999), self-assembling systems (Goodman *et al.*, 1995) or metal complexes with interesting anticancer properties (Wang *et al.*, 2000; Skurai *et al.*, 1995).



(I)

In our previous works, 1,10-phenanthroline and its derivatives have acted as chelating ligands to metal atoms (Ramezanipour *et al.*, 2004, 2005; Aghabozorg *et al.*, 2005; Moghimi, Alizadeh *et al.*, 2005; Sheshmani *et al.*, 2006) or participated in proton-transfer systems consisting of $(phenH)_2(pydc)$ [where phen is 1,10-phenanthroline and pydc is 2,6-pyridinedicarboxylate] (Moghimi, Sheshmani *et al.*, 2005) or $(creatH)(phendc)\cdot H_2O$ [where creat is creatinine and $phendcH_2$ is 1,10-phenanthroline-2,9-dicarboxylic acid] (Soleimannejad *et al.*, 2005). We report here the title proton-transfer system, (I), derived from benzene-1,2,4,5-tetracarboxylic acid and 1,10-phenanthroline.

In the structure of (I) (Fig. 1), the bond lengths and angles are within normal ranges (Allen *et al.*, 1987). According to the structural results, the asymmetric unit contains two cations, one singly charged anion, and one half of the doubly charged

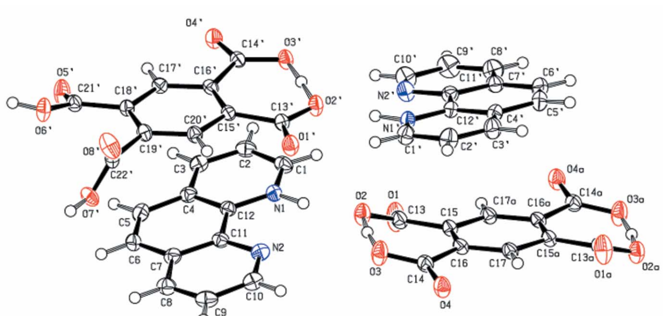


Figure 1
A view of the components of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Atoms marked with a prime are related by the symmetry code ($-x$, $-y$, $-z$).

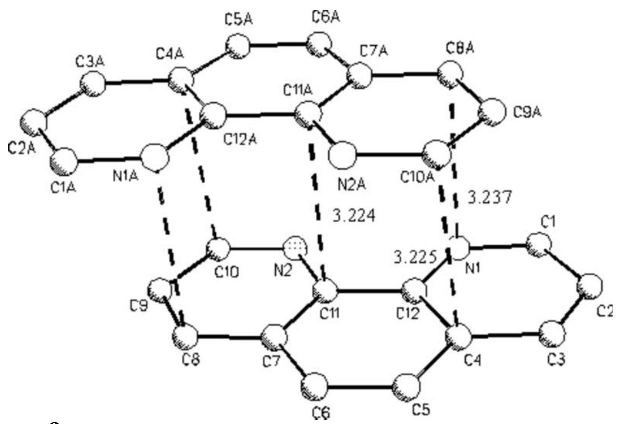


Figure 2
The π–π stacking interactions between two symmetry-related cations [the suffix A denotes atoms generated by the symmetry operator ($-x$, $-y$, $-z$)]. The average distance between the planes is 3.22 Å.

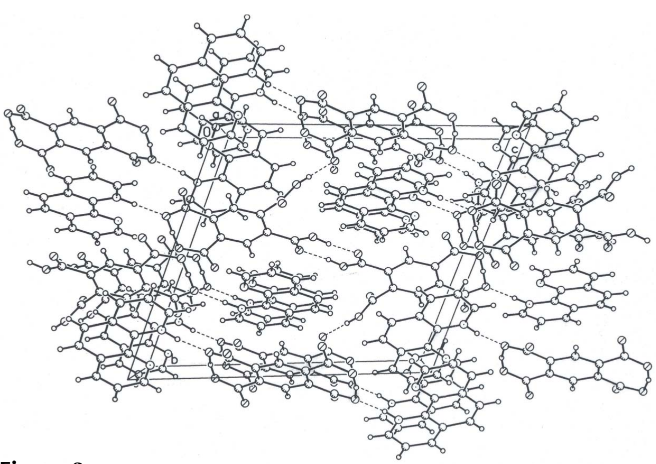


Figure 3
A packing diagram of (I). Hydrogen bonds are shown as dashed lines.

anion, which lies on an inversion center. Therefore, some of the protons of the carboxylic acid are transferred to the N atom of the 1,10-phentroline molecule. The C14—O3 [1.282 (2) Å] and C14′—O3′ [1.305 (2) Å] bond lengths are significantly different, due to strong hydrogen bonds (Table 1).

π–π Stacking interactions (Fig. 2) are observed between two symmetry-related ($-x$, $-y$, $-z$) aromatic rings of 1,10-phenanthroline, with an average distance of 3.22 Å.

As can be seen from the packing diagram (Fig. 3), intermolecular O—H⋯O and N—H⋯N hydrogen bonds (Table 1) link the ions to form a three-dimensional network. Dipole–dipole and van der Waals interactions are also effective in the packing in the crystal structure.

Experimental

The reaction of benzene-1,2,4,5-tetracarboxylic acid with 1,10-phenanthroline in a 1:2 molar ratio in tetrahydrofuran led to the formation of a white precipitate, which was filtered off and dried. The resulting powder was dissolved in water to give colourless crystals of the title compound, after four weeks at room temperature.

Crystal data

$4C_{12}H_9N_2^+\cdot 2C_{10}H_5O_8^-\cdot C_{10}H_4O_8^{2-}$	$V = 1581.1$ (3) Å^3
$M_r = 1483.26$	$Z = 1$
Triclinic, $P\overline{1}$	$D_x = 1.558$ Mg m^{-3}
$a = 8.6993$ (8) Å	Mo $K\alpha$ radiation
$b = 13.5070$ (14) Å	$\mu = 0.12$ mm^{-1}
$c = 15.1719$ (16) Å	$T = 120$ (2) K
$\alpha = 107.075$ (5)°	Prism, colourless
$\beta = 101.375$ (5)°	0.22 × 0.18 × 0.16 mm
$\gamma = 104.174$ (5)°	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	16402 measured reflections
φ and ω scans	7598 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1998)	4972 reflections with $I > 2\sigma(I)$
$T_{min} = 0.973$, $T_{max} = 0.980$	$R_{int} = 0.030$
	$\theta_{max} = 28.0°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.6P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.049$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.108$	$\Delta\rho_{max} = 0.29$ e Å^{-3}
$S = 1.07$	$\Delta\rho_{min} = -0.29$ e Å^{-3}
7598 reflections	
496 parameters	
H-atom parameters constrained	

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O2′—H2′O⋯O3′	1.18	1.23	2.402 (2)	176
N1—H1N⋯O2	0.98	1.80	2.771 (2)	171
O6′—H6′O⋯O5′^{i}	0.88	1.71	2.570 (2)	167
O7′—H7′O⋯O4^{ii}	0.82	1.76	2.583 (2)	178
O3—H3O⋯O2	1.02	1.42	2.402 (2)	159
N1′—H1′N⋯O2′	0.99	1.70	2.678 (2)	170

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

The H atoms of OH and NH groups were located in a difference synthesis and refined as riding atoms, with distances of O—H = 0.82–1.18 Å and N—H = 0.98–0.99 Å, with $U_{iso}(H) = 1.2U_{eq}$(N,O). The remaining H atoms were positioned geometrically, with C—H = 0.95 Å for aromatic H, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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