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1,10-Phenanthrolinium 2,4,5-tricarboxybenzoate

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Key indicators

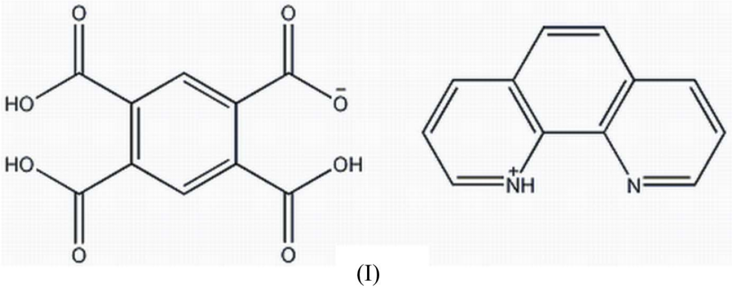
Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.003 Å
R factor = 0.038
wR factor = 0.104
Data-to-parameter ratio = 10.8

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

The title complex, $C_{12}H_9N_2^+\cdot C_{10}H_5O_8^-$ or $(Hphen)^+(H_3btc)^-$ [H_4btc = benzene-1,2,4,5-tetracarboxylic acid and phen = 1,10-phenanthroline($C_{12}H_8N_2$)], has been synthesized under hydrothermal conditions. The compound is composed of extended sheets of $[H_3btc]^-$ anions interleaved by stacks of planar $[Hphen]^+$ cations.

Comment

The coordination chemistry of aromatic polycarboxylic acids coordinated to lanthanide metal cations has been extensively investigated (Wang *et al.*, 1999; Chui *et al.*, 2001; Wang *et al.*, 2003; Zheng *et al.*, 2005). However, complexes which incorporate 1,2,4,5-benzenetetracarboxylic acid (H_4btc) and polycyclic heterocyclic ligands containing N atoms are limited (Wu *et al.*, 2002; Hu *et al.*, 2004; Wang *et al.*, 2005). In this study, we expected to obtain a complex composed of europium, H_4btc and 1,10-phenanthroline (phen) by a hydrothermal reaction. Instead, we obtained crystals of the salt $[Hphen]^+[H_3btc]^-$, (I), which exhibits fluorescent emission at 384, 405 and 423 nm in ethanol solution.



(I)

The structure of (I) is shown in Fig. 1. As in the reported hydrated complex (Arora & Pedireddi, 2003), the asymmetric unit of (I) contains one deprotonated H_4btc^- anion and one protonated $phenH^+$ cation. Within this ensemble, the anions are linked by O—H···O hydrogen bonds (Table 1) to form extended sheets (Fig. 2). The $phenH^+$ cations are arrayed on both sides of the extended sheets, forming N—H···O hydrogen bonds with the carboxylate anions (Table 1).

Experimental

A mixture of $EuCl_3\cdot 6H_2O$ (0.183 g, 0.5 mmol), H_4btc (0.127 g, 0.5 mmol), phen (0.198 g, 1 mmol) and water (3 ml) was sealed in a 23 ml Teflon reactor, heated at 363 K for 6 d and slowly cooled to room temperature. Colorless crystals were obtained after washing with water and ethanol and drying in vacuum. Analysis found: C 61.03, H 3.21, N 6.62%; calculated: C 60.84, H 3.25, N 6.45%. Melting range: 462.2–472.4 K. TGA studies showed the crystals to be stable up to 463 K. The decomposition of ligands was complete by 585 K.

Crystal data

$C_{12}H_9N_2^+\cdot C_{10}H_5O_8^-$
$M_r = 434.35$
Triclinic, $P\overline{1}$
$a = 9.4309$ (18) Å
$b = 9.6032$ (19) Å
$c = 11.710$ (2) Å
$\alpha = 69.963$ (2)°
$\beta = 83.866$ (2)°
$\gamma = 69.171$ (2)°
$V = 931.1$ (3) Å^3
$Z = 2$
$D_x = 1.549$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.12$ mm^{-1}
$T = 273$ (2) K
Block, colorless
0.30 × 0.25 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.965$, $T_{\max} = 0.976$
7468 measured reflections
3309 independent reflections
2987 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.014$
$\theta_{\max} = 25.2°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.104$
$S = 1.05$
3309 reflections
307 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2 + 0.3152P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2O···O3	0.917 (17)	1.489 (17)	2.4053 (16)	176 (3)
N2—H1N···O3$^{\rm i}$	0.95 (2)	1.77 (2)	2.6973 (16)	164.9 (19)
O7—H7*A*···O1$^{\rm ii}$	0.82	1.82	2.6308 (15)	171
O7—H7*A*···O2$^{\rm ii}$	0.82	2.67	3.2680 (17)	131
O6—H6···O5$^{\rm iii}$	0.82	1.82	2.6225 (15)	166

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

H atoms on O2 and N6 were located in a difference Fourier map and were refined isotropically. Other H atoms were placed in calculated positions (C—H = 0.93 Å and O—H = 0.82 Å) and refined using a riding model, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ and $1.5U_{\rm eq}({\rm O})$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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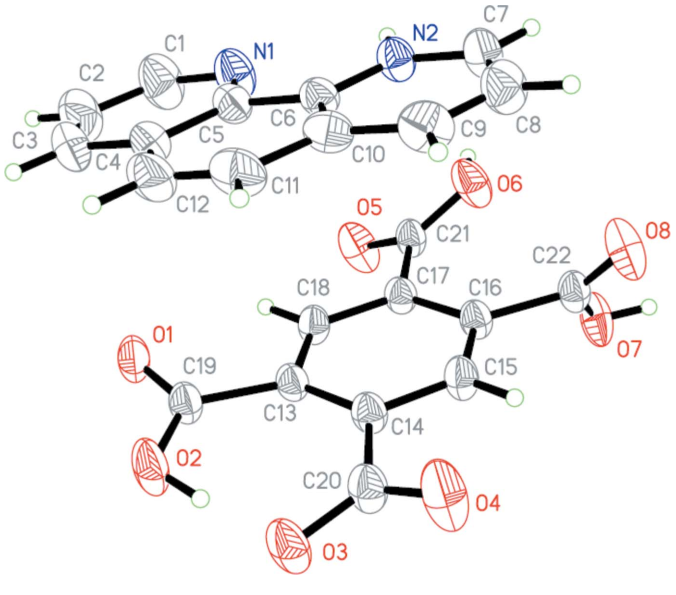

Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids.

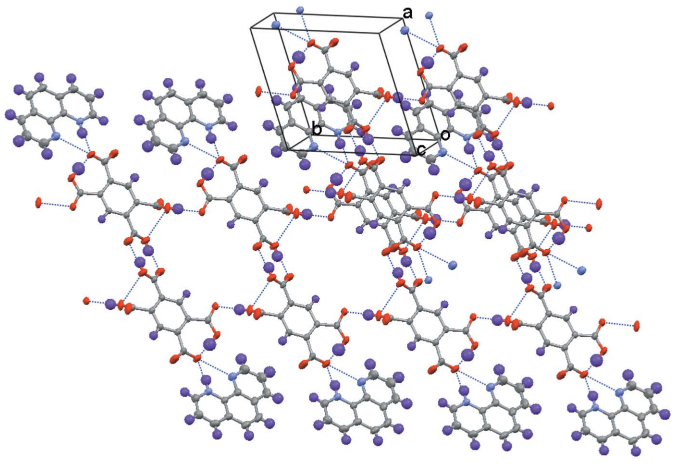

Figure 2
The packing of (I); dashed lines show the intermolecular hydrogen bonds.

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