Absorption correction:
empirical via ψ scan
(Sheldrick, 1990)
$T_{min} = 0.526$, $T_{max} = 0.667$
14 419 measured reflections
7156 independent reflections
4395 reflections with
$I > 2\sigma(I)$

$h = 0 \rightarrow 18$
$k = -14 \rightarrow 14$
$l = -23 \rightarrow 24$
2 standard reflections
every 50 reflections
intensity decay: 1.324%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.130$
$S = 1.039$
7156 reflections
443 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0616P)^2 + 2.7268P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.028$
$\Delta\rho_{max} = 1.387$ e Å^{-3}
(0.51 Å from V1)
$\Delta\rho_{min} = -0.864$ e Å^{-3}
Extinction correction: none
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

I1—V1	2.6279 (8)	V1—N4	1.951 (3)
V1—N8	1.947 (3)	V1—N2	1.960 (3)
V1—N6	1.951 (3)		
N8—V1—N6	89.11 (14)	N4—V1—N2	88.92 (14)
N8—V1—N4	160.50 (14)	N8—V1—I1	98.70 (10)
N6—V1—N4	87.76 (14)	N6—V1—I1	97.90 (10)
N8—V1—N2	88.00 (14)	N4—V1—I1	100.80 (10)
N6—V1—N2	161.57 (14)	N2—V1—I1	100.52 (10)

Data collection: *Kuma Diffractometer Software* (Kuma, 1997). Cell refinement: *Kuma Diffractometer Software*. Data reduction: *Kuma Diffractometer Software*. Program(s) used to solve structure: *SHELX97* (Sheldrick, 1997). Program(s) used to refine structure: *SHELX97*. Molecular graphics: *SHELXTL* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1259). Services for accessing these data are described at the back of the journal.

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Barium Terephthalate, a Three-Dimensional Coordination Polymer with 7:7 Cation–Anion Connectivity

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Abstract

Barium terephthalate, $[Ba\{1,4\text{-}C_6H_4(COO)_2\}]_n$, forms a three-dimensional coordination network polymer with 7:7 connectivity between the barium cations and terephthalate dianions. Each Ba atom is eight-coordinate and uses all eight oxygen lone pairs of the ligand.

Comment

The synthesis of crystalline metal coordination polymers by use of multi-functional ligands is of much recent interest, however, control of their dimensionality to achieve three-dimensional networks is often thwarted by ligation of ancillary ligands such as water. Compounds based on polybenzoate ligands are often highly hydrated and thus frequently form only one-dimensional chain or two-dimensional sheet structures. Use of hydro-thermal methods may assist loss of ancillary ligands, as shown in the case of manganese trimesate $[Mn_3(TMA)_2]$ (Gutschke et al., 1996). We have also found that the use of larger cations, such as barium or lead, which have higher coordination numbers, also promotes higher dimensionality (Chui & Williams, 1998). We report herein the structure of barium terephthalate, $[Ba\{1,4\text{-}C_6H_4(COO)_2\}]$, (I), which was crystallized at room temperature under aqueous conditions, but surprisingly is composed solely of barium cations and terephthalate anions.

(I)
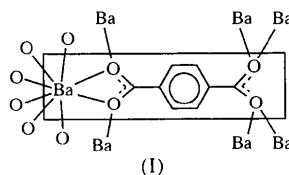
The polymer network is three-dimensional and is, we believe, the first example of an ionic structure showing 7:7 connectivity between cations and counter-anions. The asymmetric unit consists of one barium cation and one terephthalate dianion. Each terephthalate ligand has

eight lone pairs which can act as potential ligating groups and all eight are utilized (Fig. 1a) in bonding to seven different barium ions. One carboxylate (O41— C40—O42) is bidentate to one barium and monodentate to two others. The other carboxylate (O11—C10—O12) bonds in a monodentate fashion to four more bariums, using the syn and anti lone pairs of both O atoms. The bidentate carboxylate group (O41—C40—O42) is almost coplanar with the phenyl ring [dihedral angle 4.7 (1)°], whereas the (O11—C10—O12) carboxylate plane is twisted away by 31.6 (1)°. The coordination geometry about the barium ion is shown in Fig. 1(b). Just as each $[1,4-C_6H_4(COO)_2]^{2-}$ ligand is coordinated to seven barium ions, so each barium ion must be connected to seven terephthalate anions. The eight Ba— O bonds vary from 2.659 (3) to 2.944 (3) Å. The bond-valence sum (Brown & Altermatt, 1985) for barium is +2.16 for these eight contacts, confirming that there is no other chemically significant bonding between Ba and O and that the oxygen lone pairs are using the Ba^{2+} Lewis acid for stabilization efficiently.
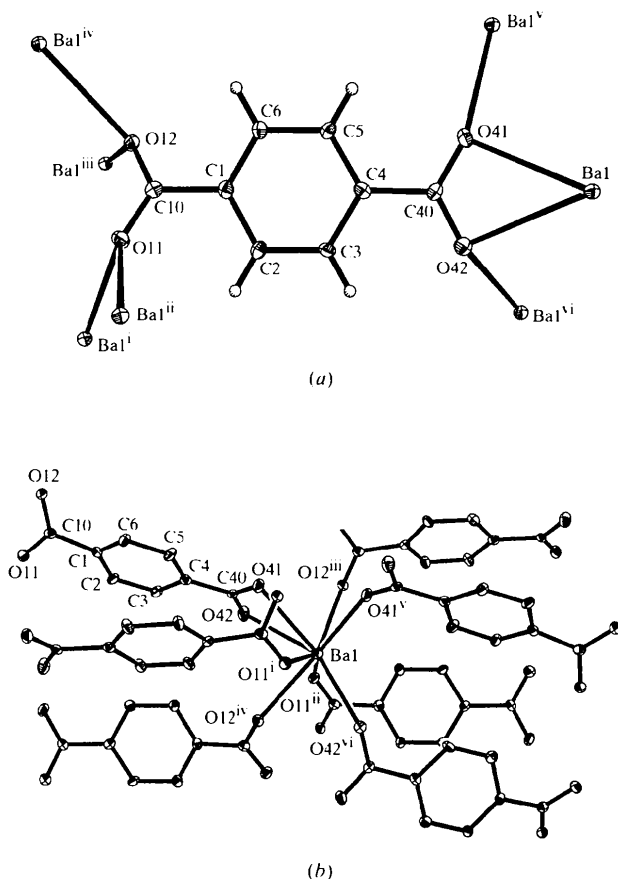

(a)

(b)

Fig. 1. Molecular structures showing 40% probability displacement ellipsoids and the coordination geometry about (a) the terephthalate ion and (b) the barium ion showing 7:7 cation–anion connectivity. The symmetry codes used are given in Table 1.

The three-dimensional polymer framework is shown in Fig. 2 looking down the [100] axis. The phenyl rings and metal carboxylates segregate into effectively alternating layers of polar ($z = 0$, $\frac{1}{2}$) and non-polar ($z = \frac{1}{4}$, $\frac{3}{4}$) groups, with the phenyl groups stacked in a roughly parallel manner along the a axis with ca 4.01 Å separation between rings.
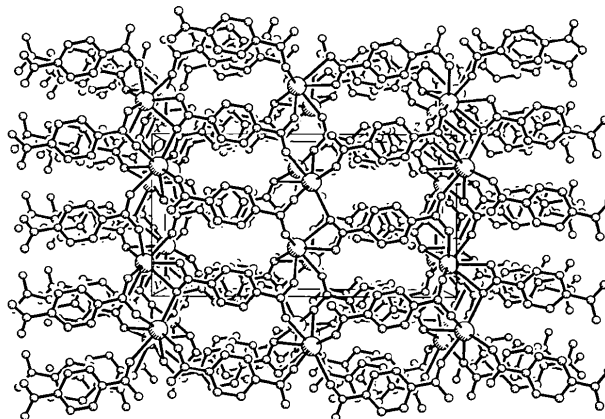

Fig. 2. The three-dimensional polymer framework viewed along [100].

In contrast to $[Ba\{1,4-C_6H_4(COO)_2\}]$, the calcium analog has been found to be a trihydrate, $[Ca\{1,4-C_6H_4(COO)_2\}(H_2O)_3]$ (Matsuzaki & Iitaka, 1972). Only a few barium benzoate complexes have been reported previously, however, $[Ba\{1,4-C_6H_4(OMe)(COO)\}_2]$ is another example of an eight-coordinate barium compound utilizing only benzoate ligands, which are coordinated in a similar manner to the O41—C40—O42 carboxylate in $[Ba\{1,4-C_6H_4(COO)_2\}]$ (Cherkezova et al., 1987). The structure of barium phthalate, $[Ba\{1,2-C_6H_4(COO)_2H\}_2]$, is known and again is not a hydrate, however, this has monoprotonated phthalate ligands, thus giving rise to a 1:2 stoichiometry (Smith, 1977). Recently, the three-dimensional structures of manganese(II) terephthalate (Hong & Do, 1997) and zinc terephthalate (Li et al., 1998) were reported which have 3(5)-methylpyrazole binding to a manganese center and methanol inside the channel, respectively.

Experimental

Barium nitrate (0.24 g, 0.9 mmol) was dissolved in water (5 ml). This was layered with a second aqueous solution (5 ml) containing terephthalic acid (0.1 g, 0.6 mmol) which had been dissolved through dropwise addition of 5 M NaOH. The pH of the final solution mixture was ca 8.0. Crystals were formed by layer diffusion over a period of one week.

Crystal data

$[Ba(C_8H_4O_4)]$	Mo Kα radiation
$M_r = 301.45$	$\lambda = 0.71073$ Å

Orthorhombic
Pbca
a = 7.792 (1) Å
b = 10.390 (1) Å
c = 18.894 (2) Å
V = 1529.6 (3) Å^3
Z = 8
D_x = 2.618 Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
θ = 2.50–17.25°
μ = 5.164 mm^{-1}
T = 293 (2) K
Block
0.1 × 0.1 × 0.1 mm
Colorless

Data collection

Siemens *P4-RA* diffractometer
$\theta/2\theta$ scans
Absorption correction:
  semi-empirical *via ψ*
  scan (*XEMP* in *XSCANS*;
  Siemens, 1994*b*)
  T_{min} = 0.583, T_{max} = 0.621
1582 measured reflections
1582 independent reflections

1262 reflections with
  $I > 2\sigma(I)$
θ_{max} = 26.5°
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 23$
3 standard reflections
  every 150 reflections
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.059
S = 1.053
1572 reflections
122 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0082P)^2$
  $+ 2.7273P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.660 e Å^{-3}
$\Delta\rho_{min}$ = −0.886 e Å^{-3}
Extinction correction: none
Scattering factors from
  International Tables for
  Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ba1—O11^i	2.712 (3)	Ba1—O41^v	2.659 (3)
Ba1—O12^{ii}	2.742 (3)	Ba1—O42^{vi}	2.745 (3)
Ba1—O11^{iii}	2.757 (3)	Ba1—O41	2.806 (3)
Ba1—O12^{iv}	2.868 (3)	Ba1—O42	2.944 (3)
O11^i—Ba1—O11^{iii}	148.50 (6)	O42^{vi}—Ba1—O12^{iv}	134.55 (9)
O41^v—Ba1—O11^i	135.10 (1)	O11^{iii}—Ba1—O12^{iv}	135.93 (9)
O41^v—Ba1—O12^{ii}	148.10 (1)	O42^{vi}—Ba1—O42	151.71 (6)
O42^{vi}—Ba1—O41	140.7 (1)	O11^{iii}—Ba1—O42	100.65 (9)
O41^i—Ba1—O12^{ii}	69.6 (1)	O41—Ba1—O42	45.21 (9)
O12^{ii}—Ba1—O12^{iv}	139.43 (9)		

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

A relatively small crystal was chosen to minimize absorption effects.

Data collection: *XSCANS* (Siemens, 1994*b*). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994*a*).

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Aqua(4,4'-dimethyl-2,2'-bipyridine-*N,N'*)-(malonato-*O,O'*)copper(II) Dihydrate

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Abstract

The title compound, [Cu(C$_3$H$_2$O$_4$)(C$_{12}$H$_{12}$N$_2$)(H$_2$O)].2H$_2$O, lies on a crystallographic mirror. The Cu^{II} ion in the complex has a slightly distorted square-pyramidal