

Bis(2-amino-1*H*-benzimidazol-3-ium) tetrakis(μ -but-2-enoato)- $\kappa^4 O:O'$;- $\kappa^3 O,O':O$; $\kappa^3 O:O,O'$ -bis[bis(but-2-enoato)- $\kappa^2 O,O'$]holmium(III)

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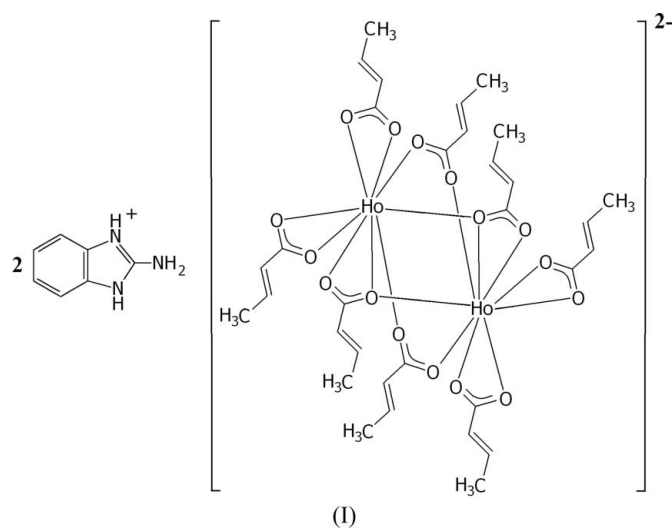
The title ionic compound, $(C_7H_8N_3)_2[Ho_2(C_4H_5O_2)_8]$, is constructed from two almost identical independent centrosymmetric anionic dimers balanced by two independent 2-amino-1*H*-benzimidazol-3-ium (Habim⁺) cations. The asymmetric part of each dimer is made up of one Ho^{III} cation and four crotonate (crot or but-2-enoate) anions, two of them acting in a simple η^2 -chelating mode and the remaining two acting in two different $\mu_2:\eta^2$ fashions, *viz.* purely bridging and bridging–chelating. Symmetry-related Ho^{III} cations are linked by two Ho–O–Ho and two Ho–O–C–O–Ho bridges which lead to rather short intracationic Ho \cdots Ho distances [3.8418 (3) and 3.8246 (3) Å]. In addition to the obvious Coulombic interactions linking the cations and anions, the isolated $[Ho_2(crot)_8]^{2-}$ and Habim⁺ ions are linked by a number of N–H \cdots O hydrogen bonds, in which all N–H groups of the cation are involved as donors and all (simple chelating) crot O atoms are involved as acceptors. These interactions result in compact two-dimensional structures parallel to (110), which are linked to each other by weaker π – π contacts between Habim⁺ benzene groups.

Comment

Carboxylate-bridged homonuclear systems constitute a popular target in structural chemistry, mainly due to the coordination versatility which these ligands introduce. This allows for a diversity of frameworks of varied complexity and dimensionality, from simple zero-dimensional isolated dimeric units to tightly bound three-dimensional structures, with a concomitant diversity in physical properties, leading to applications in fields as diverse as ion exchange, catalysis, molecular absorption, optics, electronics *etc.* (Ma *et al.*, 2000;

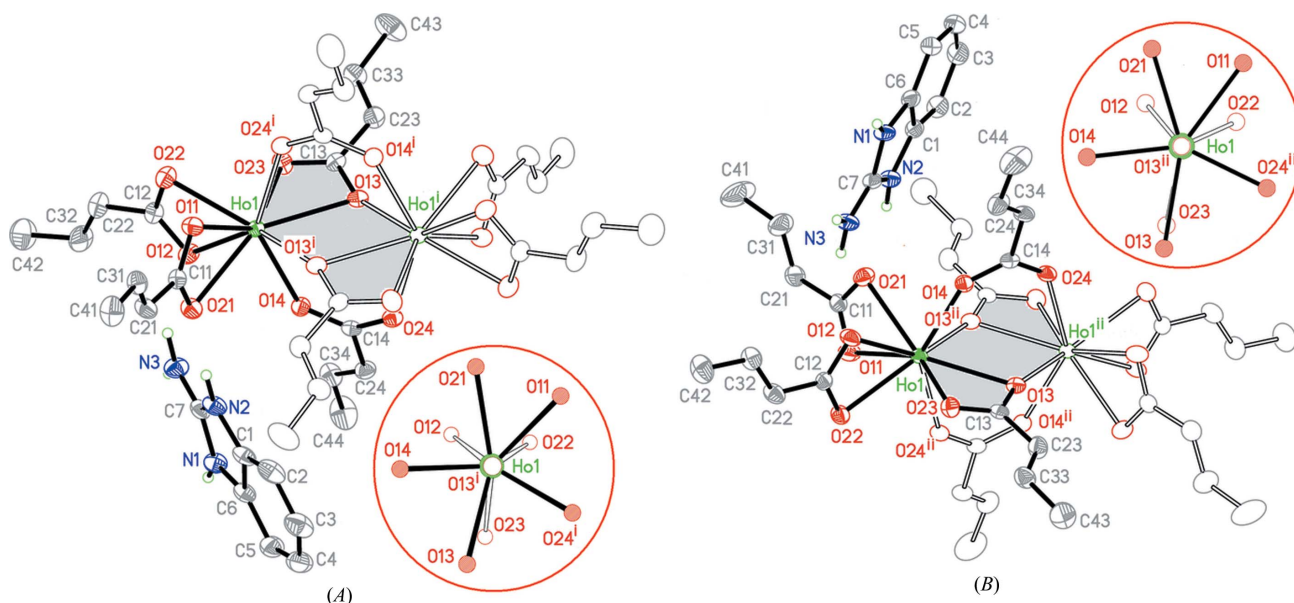
Wang *et al.*, 2002; Xu *et al.*, 2002; Benelli & Gatteschi, 2002; Pan *et al.*, 2004).

We have for some time focused our attention on the efficiency of crotonic acid (C_3H_5COOH , hereinafter denoted Hcrot; systematic name: but-2-enoic acid) in coupling Ln^{III} ions, and as a result we have described the synthesis and the structural and (occasionally) magnetic characterization of a number of crotoate–lanthanide complexes obtained in conjunction with a variety of nitrogenous bases (NB), such as diaminopurine, adenine *etc.*, which proved quite efficient in promoting crystal stabilization through their inclusion as neutral cocrystallization agents (Atria *et al.* 2009, 2012*a,b*), as counter-ions (Atria, Morel *et al.*, 2011) or even as coordinating ligands (Atria, Corsini *et al.*, 2011; Atria, Garland & Baggio, 2011).



In pursuit of our synthetic efforts in this line, we succeeded in generating a new member of the Ln–crot–NB family, this time with Ln = Ho and NB = 2-amino-1*H*-benzimidazol-3-ium (hereinafter Habim⁺), and which we present herein, *viz.* the dinuclear ionic complex formulated as $(Habim)_2[Ho_2(crot)_8]$, (I). The crystal structure is built from two almost identical centrosymmetric $[Ho_2(crot)_8]^{2-}$ anionic dimers complemented by two independent Habim⁺ cations, providing for charge balance and structural cohesion. These four different groups in the structure associate in two similar cation–anion pairs which we differentiate with the suffixes *A* and *B* (as shown in Fig. 1). To facilitate comparison, equivalent atoms in different groups have been given the same number.

Each independent ‘half-dimer’, *A* or *B* in Fig. 1, is made up of one Ho^{III} cation and four crot anions, two of which act in a simple η^2 -chelating mode (crot1 and crot2), while the remaining two bind in two different $\mu_2:\eta^2$ fashions, *viz.* purely bridging (crot4) and bridging–chelating (crot3). The distribution of Ho–O distances is rather similar in both dimeric units, displaying ranges of 2.290 (2)–2.523 (2)/2.305 (2)–2.531 (2) Å [in what follows, values separated by a solidus (/) are presented in *A/B* order]. Selected coordination details are given in Table 1.


Figure 1

The structure of (I), grouped into cation–anion pairs *A* and *B*. For clarity, the suffixes *A* and *B* are not explicitly shown in the labels, but are defined as part of each figure. Independent (symmetry-related) atoms are shown with solid (hollow) bonds and filled (empty) displacement ellipsoids, drawn at the 40% probability level. The shaded areas denote plane 1; see *Comment* and Table 2. Insets: the coordination assembly of the Ho^{III} cation in each group, where solid (hollow) balls and sticks represent different height levels. [Symmetry codes: (i) $-x + 1, -y, -z + 2$; (ii) $-x, -y + 1, -z + 1$].

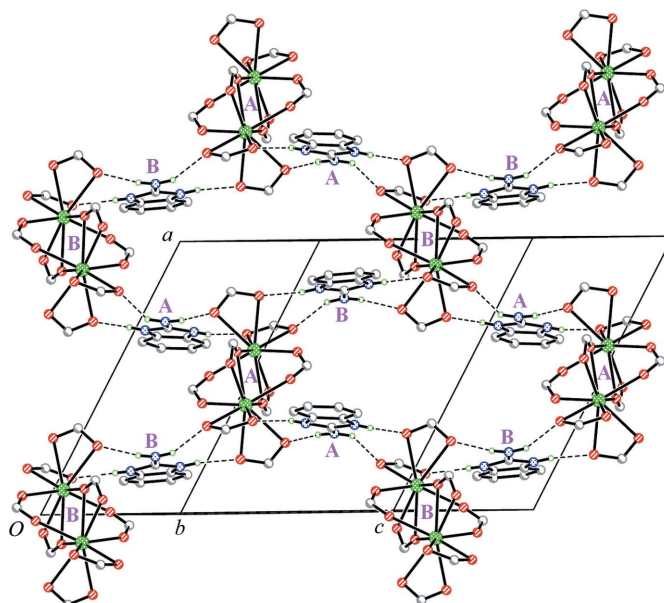
The insets in Fig. 1 show the very similar HoO₉ coordination assemblies, which consist of five O atoms in equatorial positions and which describe a rather planar structure [mean deviations = 0.043 (2)/0.025 (2) Å], capped by one O atom above the plane and a triangular array on the opposite side. The Ho^{III} cation, in turn, lies 0.535 (2)/0.539 (2) Å below the pentagonal equatorial mean plane.

Although four isolated Ln(RCOO)₈ nuclei of this kind having different Ln centres have been reported in the literature [Cambridge Structural Database (CSD; Allen, 2002) refcodes EXUXIE (Ln = Eu), CUMTOU (Ln = La), VUJPEV (Ln = Gd) and RAPCOB (Ln = Lu) (Li & Hu, 2005)], none of them features Ho^{III} as the cation, making (I) the first complex to display such an Ho(RCOO)₈ nucleus. Nonetheless, there are structures with similar bridging schemes around Ho centres (*viz.* two pairs of Ho–O–Ho and Ho–O–C–O–Ho bridges), which in the present case lead to Ho···Ho distances of 3.8418 (3)/3.8246 (3) Å, at the lower limit of the range reported for Ho···Ho distances in this particular bridging configuration. A search of the CSD retrieved 14 structures of this type, with Ho···Ho distances ranging from 3.8559 (9) (CSD refcode NADBIF; Guo *et al.*, 2010) to 4.2422 (15) Å (CSD refcode PUKFUW; Legendziewicz *et al.*, 1989). Therefore, none exhibits a shorter Ho···Ho distance than those herein reported.

As stated above, the dimeric units *A* and *B* are very similar, not only in their metrics (Table 1) but also in some particular geometric details. Each presents four well-defined coordination planes, denoted 1–4, and these are presented in Table 2 with their maximum deviations from planarity. The most conspicuous plane is 1, shown as a shaded area in Fig. 1; it halves each dimeric unit, acting as a ‘basal’ plane, with the remaining three planes (2–4) disposed very nearly perpendi-

cular to it, subtending dihedral angles which differ from the ideal value of 90° by less than 4.1 (2)/2.5 (2)°.

The unbound Habim⁺ counter-anions do not show any unexpected features. This form of the aminobenzimidazole unit, present in (I), is frequently adopted by the molecule in the solid state: out of 25 structures found in the CSD containing the moiety in any of its forms, in 11 it appears protonated, while in 12 it behaves as a coordinated ligand,


Figure 2

A packing view of (I), showing the hydrogen-bonded two-dimensional structure. Each [Ho₂(crot)₈]²⁻ + Habim⁺ group is identified by its *A* or *B* suffix. For clarity, crot groups are represented by their carboxylate end only. H atoms attached to C atoms have been omitted.

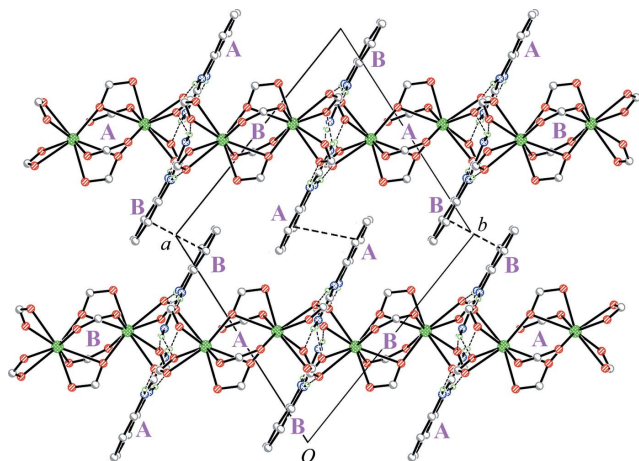


Figure 3
A packing view of (I), drawn along [001], showing the planes in projection. Note the interdigitation of neighbouring Habim⁺ cations, linking vicinal planes through π - π contacts. A and B coding is as in Fig. 2.

either through both imidazole N atoms (three entries) or simply through one of them (nine entries). Only in two structures does aminobenzimidazole appear as a neutral uncoordinated species [CSD refcodes DIQLEU (Wulff-Molder & Meisel, 1999) and HUZSEA (El-Medani *et al.*, 2003)].

The crystal packing in (I) involves a mixture of different interactions of varied type and strength. In addition to the obvious Coulombic forces between cations and anions, the isolated $[\text{Ho}_2(\text{crot})_8]^{2-}$ and Habim⁺ ions are linked by a number of N—H...O hydrogen bonds, in which all eight Habim⁺ N—H groups are involved as donors and all eight crot O atoms corresponding to the purely chelating carboxylate groups act as acceptors (Table 3). Each Habim⁺ cation (either A or B) links two dimers of a different (A,B) kind, with two hydrogen bonds at each side. These N—H...O hydrogen bonds are particularly even in both disposition and strength [$\text{N}\cdots\text{O} = 2.722(4)\text{--}2.889(4)\text{ \AA}$] and define compact two-dimensional structures parallel to (110) (Fig. 2). The regularity of the hydrogen-bonding scheme is revealed by the loop structure it gives rise to, defined by four identical $R_2^2(8)$ rings (Bernstein *et al.*, 1995) of general scheme $\cdots\text{O}—\text{Ho}—\text{O}\cdots\text{H}—\text{N}—\text{C}—\text{N}—\text{H}\cdots$. When viewed in projection, these structures show an exactly planar core of dimeric centroids [with inversion centres of general coordinates $r(n_1, n_2) = (\frac{1}{2}, 0, 0) + n_1(\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}) + n_2(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$, where n_1 and n_2 are integers], while the Habim⁺ cations stretch outwards on both sides and interdigitate with similar ones in adjacent planes, giving rise to π - π contacts between benzene rings which connect the planes along [110] (Table 4).

Bond valence (BV) analysis using the recently revised coefficients R_{ij} from Trzesowska *et al.* (2004) led to BV sums of 3.045 (Ho1A) and 2.979 (Ho1B), consistent with the Ho^{III} oxidation state of the cations. Similar results were obtained for three of the closely related isocoordinated $\text{Ln}(\text{RCOO})_8$ structures mentioned above (Ln = La, Er and Gd). However, a rather puzzling result was provided by comparison with the fourth compound of the series with Ln = Lu [CSD refcode

RAPCOB, (II); Li & Hu, 2005], where the core around the Lu^{III} cation, very similar to that around the Ho^{III} centres in (I), is built up by 2-hydroxyphenylacrylate groups. These differ from crot only in that the terminal methyl group in the latter is replaced by a phenyl ring, so we expected similar cation behaviour. However, BV calculations gave an extremely low BV sum of 2.371 for Lu in (II), suggesting much lower involvement of the Lu^{III} cation in coordination than was found for Ho in (I). A possible reason for this intriguing effect is the fact that the terminal groups are quite different electronically, methyl groups being electron-releasing while phenyl rings are, in contrast, electron-withdrawing.

Experimental

Crotonic acid (0.5165 g, 6 mmol) dissolved in water (30 ml) was added to a solution of Ho_2O_3 (0.3778 g, 1 mmol) in water (300 ml). The resulting solution was refluxed for 30 min. A suspension of 2-aminobenzimidazole (0.1332 g, 1 mmol) in ethanol (30 ml) was added to this solution. The resulting mixture was refluxed for 24 h, filtered and left to evaporate slowly at room temperature. Crystals of (I) suitable for structural analysis were obtained after three weeks.

Crystal data

$(\text{C}_7\text{H}_8\text{N}_3)_2[\text{Ho}_2(\text{C}_4\text{H}_5\text{O}_2)_8]$	$\gamma = 63.700(1)^\circ$
$M_r = 1278.83$	$V = 2624.0(3)\text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 14.2688(8)\text{ \AA}$	Mo $K\alpha$ radiation
$b = 15.0608(9)\text{ \AA}$	$\mu = 3.06\text{ mm}^{-1}$
$c = 15.7276(9)\text{ \AA}$	$T = 150\text{ K}$
$\alpha = 66.226(1)^\circ$	$0.26 \times 0.13 \times 0.05\text{ mm}$
$\beta = 63.654(1)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	21803 measured reflections
Absorption correction: multi-scan (SADABS in SAINT-NT; Bruker, 2002)	11159 independent reflections
$T_{\min} = 0.60, T_{\max} = 0.86$	9348 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.070$	$\Delta\rho_{\text{max}} = 1.97\text{ e \AA}^{-3}$
$S = 1.05$	$\Delta\rho_{\text{min}} = -0.59\text{ e \AA}^{-3}$
11159 reflections	
663 parameters	
10 restraints	

Table 1

Selected interatomic distances (\AA).

Ho1A—O14A	2.290(2)	Ho1B—O13B ⁱⁱ	2.305(2)
Ho1A—O13A ⁱ	2.316(2)	Ho1B—O14B	2.308(2)
Ho1A—O24A ⁱ	2.321(2)	Ho1B—O24B ⁱⁱ	2.309(2)
Ho1A—O23A	2.394(2)	Ho1B—O23B	2.417(2)
Ho1A—O11A	2.438(2)	Ho1B—O12B	2.422(2)
Ho1A—O22A	2.446(2)	Ho1B—O21B	2.458(2)
Ho1A—O12A	2.467(2)	Ho1B—O22B	2.476(2)
Ho1A—O21A	2.483(2)	Ho1B—O11B	2.492(3)
Ho1A—O13A	2.523(2)	Ho1B—O13B	2.531(2)
Ho1A...Ho1A ⁱ	3.8418(3)	Ho1B...Ho1B ⁱⁱ	3.8246(3)

Symmetry codes: (i) $-x + 1, -y, -z + 2$; (ii) $-x, -y + 1, -z + 1$.

Table 2

Relevant coordination planes in (I).

Plane	Atoms in plane	Deviations (A/B) (Å)
1	C13/O13/O23/Ho1/ [C13/O13/O23/Ho1] ⁱⁱⁱ	0.078 (2)/0.031 (2)
2	C14/O14/O24/Ho1/ [C14/O14/O24/Ho1] ⁱⁱⁱ	0.092 (2)/0.084 (2)
3	C11/O11/O21/Ho1	0.031 (2)/0.012 (2)
4	C12/O12/O22/Ho1	0.012 (2)/0.01 (2)

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

All H atoms were originally found in a difference Fourier map but were treated differently in the refinement. C-bound H atoms were repositioned in their expected positions and thereafter allowed to ride (aromatic C–H = 0.95 Å and methyl C–H = 0.98 Å), while N-bound H atoms were refined with restrained distances of N–H = 0.88 (1) Å and, for the NH₂ groups, H···H = 1.40 (2) Å. In all cases, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl groups and $1.2U_{\text{eq}}(\text{C}, \text{N})$ otherwise. In the final difference map, the highest peak lies 1.24 Å from atom Ho1B and the deepest hole 0.92 Å from the same atom. Competitive refinements with the metals set to be Dy or Er gave results which were indistinguishable from those with the metal as Ho.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM3118). Services for accessing these data are described at the back of the journal.

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Table 3

Hydrogen-bond geometry (Å, °).

D–H···A	D–H	H···A	D···A	D–H···A
N1A–H1AA···O22B	0.87 (3)	1.93 (3)	2.804 (4)	174 (4)
N2A–H2AA···O21A	0.89 (4)	1.97 (4)	2.849 (4)	171 (4)
N3A–H3A2···O11B	0.87 (2)	2.02 (2)	2.860 (4)	162 (4)
N3A–H3A1···O12A	0.87 (5)	1.95 (4)	2.820 (4)	172 (3)
N1B–H1BA···O22A ⁱⁱⁱ	0.87 (3)	1.87 (3)	2.722 (4)	170 (4)
N2B–H2BA···O21B	0.87 (2)	1.90 (2)	2.733 (4)	159 (3)
N3B–H3B1···O12B	0.87 (2)	2.03 (2)	2.889 (4)	168 (3)
N3B–H3B2···O11A ⁱⁱⁱ	0.88 (3)	1.94 (4)	2.814 (4)	174 (4)

 Symmetry code: (iii) $x, y, z - 1$.

Table 4
 π – π interactions (Å, °) for (I).

ccd is the centroid-to-centroid distance (distance between ring centroids), ipd is the interplanar distance (mean distance from one plane to the neighbouring centroid) and sa is the slippage angle (mean angle subtended by the intercentroid vector to the plane normal); for more details, see Janiak (2000). Cg1 and Cg2 are the centroids of the C1A–C6A and C1B–C6B rings, respectively.

Group1···group2	ccd	ipd	sa
Cg1–Cg1 ⁱ	3.986 (3)	3.524 (2)	27.9 (2)
Cg2–Cg2 ⁱⁱ	3.587 (3)	3.379 (2)	19.6 (2)

 Symmetry codes: (i) $-x, -y, -z + 2$; (ii) $-x + 1, -y + 1, -z$.

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