

## An Infinite Ladder Structure of Alternating, Fused $K_2N_2$ Rhomboids and $KN_2$ Triangles: Synthesis and Crystallographic Characterisation of Benzotriazolotopotassium-HMPA (HMPA = hexamethylphosphoric triamide)

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Benzotriazolotopotassium-HMPA, a rare example of an alkali metal benzotriazole derivative, has been synthesised and shown by an X-ray diffraction study to have an intricate, polymeric ladder arrangement made up of alternating, fused  $K_2N_2$  rhomboids and  $KN_2$  triangles.

Benzotriazole (BTAH) **1** has attracted much interest because of its technological importance, especially its use in corrosion inhibition of metallic copper and alloys thereof.<sup>1</sup> Structural studies of metal compounds containing BTAH or its deprotonated anionic form  $BTA^-$ , provide insight into the possible ligating modes of this ligand. With this coordinative knowledge, the complicated surface chemistry involved in corrosion inhibition may become clearer. Several relevant crystal structures, mostly with transition metal atoms (*e.g.* Cu,<sup>2</sup> Hg,<sup>3</sup> Os<sup>4</sup>), have appeared: a recent review is available.<sup>5</sup> However, to the best of our knowledge, the early main group block of metals in which we are particularly interested, have until now been overlooked in this regard. Lithium was the first such metal to be investigated in this connection by us, but so far our attempts to crystallise a  $BTA^-$  derivative have proved fruitless. In contrast, switching attention to the heavier alkali metal potassium has allowed us to successfully synthesise and crystallographically characterise the hexamethylphosphoric triamide (HMPA) adduct of benzotriazolotopotassium **2**, and we report our findings here. From the point of view of the metal and of the heterocyclic ligand, the crystal structure is unique in exhibiting an infinite ladder framework of alternating, fused  $K_2N_2$  rhomboids and  $KN_2$  triangles.

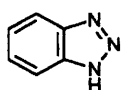
A rather delicate procedure was followed in the synthesis and crystallisation of adduct **2**. Thus, freshly-sublimed and vacuum-dried BTAH (10 mmol) was dissolved in HMPA (20

mmol). This solution was then added to a liquid nitrogen cooled suspension of  $Bu^nK$  (10 mmol) in hexane, protected by an argon blanket. Reaction proceeded slowly on allowing the mixture to reach room temp. and on further heating to about 50 °C for 30 min, at which stage a white suspension was visible. Hexane solvent was subsequently removed *in vacuo*. Addition of more HMPA (90 mmol) to the residue, which was then heated to 70 °C, gave a homogeneous solution. Finally, cooling this solution to 45 °C and keeping it at this temperature for 24 h, afforded long, colourless needles of **2**.<sup>†</sup> Microcrystalline samples were obtained if the solution temperature fell below 45 °C.

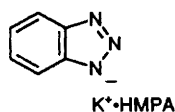
Fig. 1 shows a trinuclear section within the crystal structure<sup>‡</sup> which highlights the local coordination geometries of the  $K^+$  cations and  $BTA^-$  anions. The six coordinate environment of the metal involves three  $BTA^-$  anions and one HMPA

<sup>†</sup> Satisfactory analyses (C, H, K, N) were obtained.

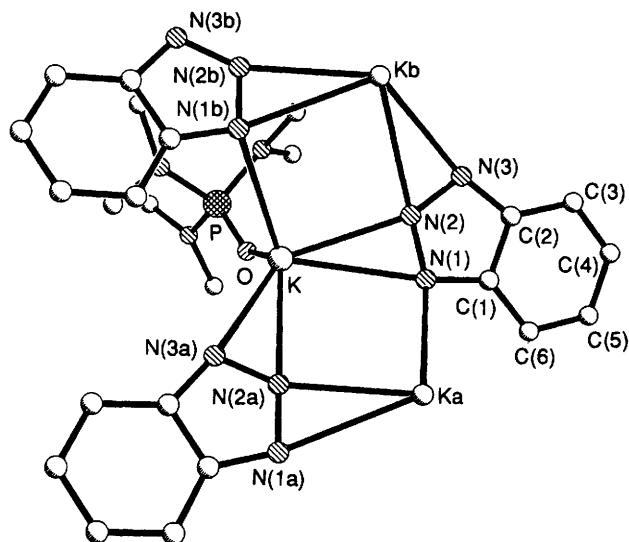
<sup>‡</sup> Crystal data for **2**:  $C_{12}H_{22}KN_6OP$ ,  $M = 336.4$ , orthorhombic, space group  $P2_12_12_1$ ,  $a = 6.340(4)$ ,  $b = 12.606(6)$ ,  $c = 21.326(12)$  Å,  $U = 1704(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.311$  g cm<sup>-3</sup>. 2992 independent reflections were measured on a Siemens AED2 diffractometer using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å),  $\mu(\text{Mo-K}\alpha) = 0.41$  mm<sup>-1</sup>, with  $\omega/\theta$  scans and on-line profile fitting,<sup>11</sup>  $F(000) = 712$ . Structure solution was by direct methods, refinement by full-matrix least-squares on  $F^2$  for all independent reflections.<sup>12</sup>  $wR2$  (all data) =  $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2} = 0.1105$ , conventional  $R$  [on  $F$  values for 2674 reflections with  $F_o^2 > 2\sigma(F_o^2)$ ] = 0.0386. Atomic coordinates, bond lengths and angles, and atomic displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**1**



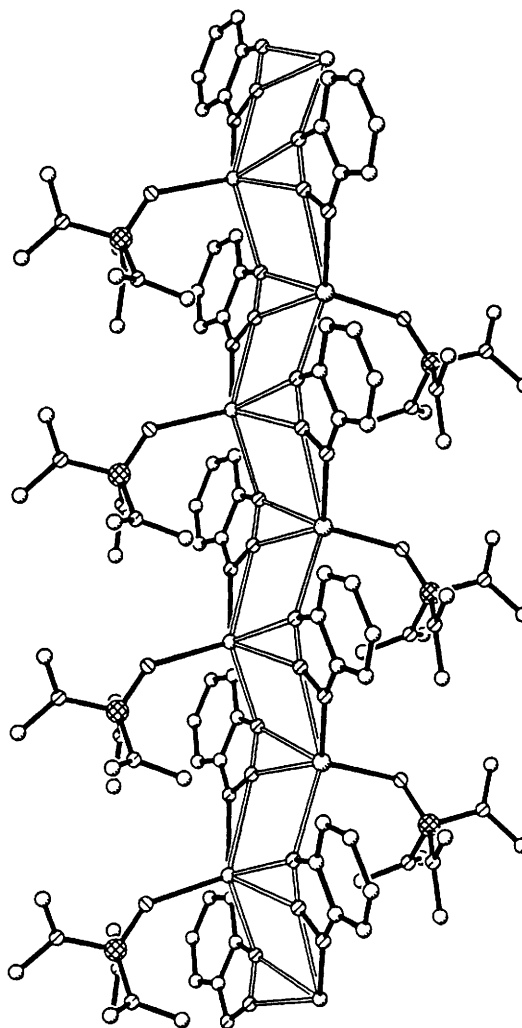
**2**



**Fig. 1** View of a trinuclear section of **2**, without hydrogen atoms and with important atoms labelled. Key dimensions: K–O 2.616(3), K–N(2) 2.745(4), K–N(1) 2.938(4), K–N(2a) 2.898(4), K–N(3a) 2.766(4), K–N(1b) 2.901(4) Å; O–K–N(2) 105.69(9), O–K–N(3a) 118.22(9), N(2)–K–N(3a) 128.78(9), O–K–N(2a) 123.98(9), N(2)–K–N(2a) 105.54(9), O–K–N(1b) 104.96(9), N(2)–K–N(1b) 88.03(9), N(3a)–K–N(1b) 103.80(9), N(2a)–K–N(1b) 121.40(9), O–K–N(1) 104.87(9), N(3a)–K–N(1) 111.18(9), N(2a)–K–N(1) 84.52(9), N(1b)–K–N(1) 113.99(8)°.

molecule. Two of the anions bind in a didentate manner through N(1), N(2) and N(2a), N(3a); the other in a monodentate manner through N(1b) (range of K–N bond lengths, 2.745–2.938 Å). HMPA assumes a terminal, monodentate role through its oxygen atom, in contrast to the  $\mu_2$ - and  $\mu_3$ -bonding roles it displays in the recently reported  $[(KSCN)_3 \cdot (HMPA)_5]$ :<sup>6</sup> the K–O bond is consequently much shorter in **2** [2.616(3) *cf.* 2.748(8) and 2.712(5) Å, respectively]. Three K<sup>+</sup> cations occupy the coordination sphere of a single BTA<sup>−</sup> anion, accounting for five K–N contacts in total. Here, therefore, the polydentate anion functions simultaneously as a didentate ligand to two K<sup>+</sup> cations [through donor atom pairs N(1), N(2) and N(2), N(3)], and as a monodentate ligand to a third cation [through donor atom N(1)]. A comparison can be made with the structure of polynuclear benzotriazolothallium<sup>7</sup> but only insofar as its BTA<sup>−</sup> anions are also tris-coordinated by metal [Tl<sup>+</sup>] cations. Significantly, however, the six Tl–N contacts (per Tl<sup>+</sup> centre) fall into two distinct categories (three short and three long, at distances of 2.725–2.792 and 3.271–3.326 Å, respectively; largest difference, 0.601 Å), whereas the five K–N contacts (per K<sup>+</sup> centre) in **2** have similar distances to each other (largest difference, 0.193 Å). Bond distances within the BTA<sup>−</sup> anions are generally shorter, though only marginally so, in **2** [*e.g.* N(1)–N(2), 1.351(4), C(1)–N(1), 1.363(4), C(1)–C(2), 1.401(4) Å; *cf.* in the Tl example,<sup>7</sup> 1.362(6), 1.381(7), 1.403(7) Å respectively], implying that the anions attached to K<sup>+</sup> carry a slightly higher charge (close to the formal value of −1), in line with the greater electropositivity of K *cf.* Tl. In **2**, the mode of coordination has some bearing on these distances as bonds involving the three-coordinate N(3) atom [N(2)–N(3), C(2)–N(3)] are slightly shorter than corresponding ones involving four-coordinate N(1) [N(1)–N(2), C(1)–N(1)] [*i.e.* 1.334(4), 1.356(4) Å *cf.* 1.351(4), 1.363(4) Å, respectively].

The extended nature of the crystal structure of **2** is shown in Fig. 2. Its most salient feature is the infinite ladder framework, made up of alternating fused  $K_2N_2$  rhomboids and  $KN_2$  triangles, running through the centre of the structure. There appears to be no precedent in the literature for this type of arrangement, nor indeed have there been any reports of



**Fig. 2** View showing the ladder-like nature of the extended structure

simple K–N ladders, though such constructions are known with Li<sup>8,9</sup> and with Na<sup>10</sup>. Key aspects of the structure are now discussed. All K<sup>+</sup> cations lie in the same plane. The BTA<sup>−</sup> anions are essentially planar. Mean internal bond angles in the  $K_2N_2$  rhomboids are 86.28 and 93.21° for K and N respectively. These approximately planar (RMS deviation, 0.096 Å) rhomboids are separated by  $KN_2$  triangles with acute K corners [internal bond angle, 27.23(8) *cf.* 68.38(15) and 84.4(2)° at the N corners of the triangle]. Where the rhomboids meet these triangles, the dihedral angles are 42.8° between the [K, N(1), N(2)] and [K, N(1), K(a), N(2a)] planes and 14.0° between the [K, N(1), K(a), N(2a)] and [K(a), N(1a), N(2a)] planes, which accounts for the zigzag appearance of the stepladder. The BTA<sup>−</sup> anions alternate above and below the ladder framework (dihedral angle between [K, N(1), N(2)] and BTA planes, 15.6°), as do the HMPA ligands [bond angles: O–K–N(1), 104.87(9); O–K–N(2), 105.69(9)°]. Additional  $KN_2$  triangles [internal bond angles at K, 27.13(7), at N, 70.9(2) and 81.9(2)°] fused onto every second KN ladder edge are a consequence of the terminal attachment of the monodentate N(3) atoms. The structure is non-centrosymmetric and the ladder lies along the crystallographic  $2_1$  screw axis along *a*.

On the evidence of structure **2** the BTA ligand is obviously a flexible ligand as implied by the coordination geometry in the K-complex.

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