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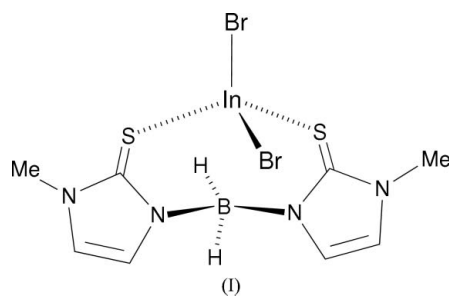
## Key indicators

Single-crystal X-ray study  
 $T = 296$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.008$  Å  
 $R$  factor = 0.030  
 $wR$  factor = 0.083  
Data-to-parameter ratio = 17.5For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.**[Bis(3-methyl-2-thioxo-2,3-dihydro-1*H*-imidazolyl)borato- $\kappa^2$ S,S']dibromoindium(III)**

The structure of the title compound,  $[\text{InBr}_2(\text{C}_8\text{H}_{12}\text{N}_4\text{BS}_2)]$ , the first bis(mercaptoimidazolyl)borate ( $\text{Bm}^{\text{Me}}$ ) complex of indium to be structurally characterized, has been determined by single-crystal X-ray diffraction. The four-coordinate In atom displays a distorted tetrahedral geometry in the solid state and is surrounded by the two thione groups of a  $\text{Bm}^{\text{Me}}$  ligand and two bromides, with an average In—Br bond distance of 2.494 Å. The presence of a crystallographically imposed mirror plane results in the observation of a unique In—S bond length of 2.4407 (11) Å.

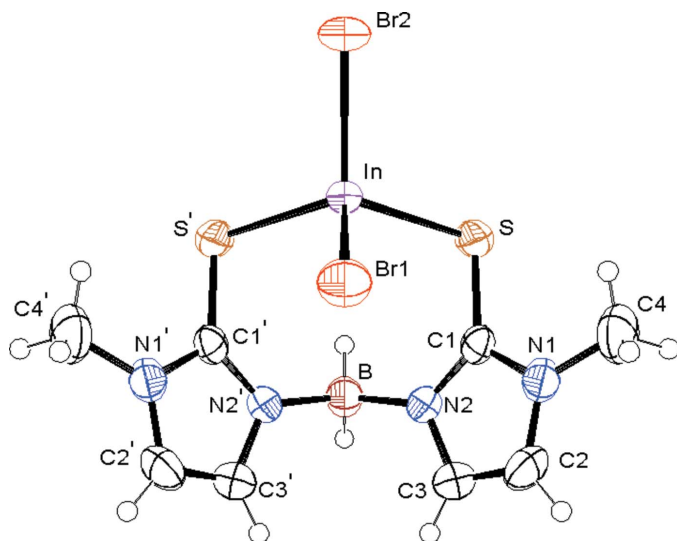
## Comment

Interest in the chemistry of indium(III) with sulfur donor ligands, including thioureas, thiolates and dithiocarbamates, has often been motivated by the search for suitable molecular precursors for the preparation of optoelectronic and photovoltaic materials (Barron, 1995; Dutta *et al.*, 2002). The anionic bis(mercaptoimidazolyl)borate ( $\text{Bm}^{\text{R}}$ ) ligand system (Kimblin *et al.*, 1997), which features two thione ( $\text{C}=\text{S}$ ) donor groups for coordination to a metal center, is increasingly being used to prepare complexes in a well defined 'soft' coordination environment. Seeking to expand the number of main group metal compounds containing these soft ligands, currently limited to a series of thallium(I) derivatives  $\text{Tl}(\text{Bm}^{\text{R}})$  (Alvarez *et al.*, 2004), we set out to prepare indium(III) complexes supported by  $\text{Bm}^{\text{R}}$  ligands. We report here the molecular structure of dibromo[bis(2-mercapto-1-methylimidazolyl)borate]indium(III), (I), which constitutes the first indium bis(mercaptoimidazolyl)borate complex to be synthesized and structurally characterized. In addition,  $\text{In}(\text{Bm}^{\text{Me}})\text{Br}_2$  is also the first four-coordinate indium compound displaying an  $[\text{InS}_2\text{Br}_2]$  core. The synthesis and structure of the related tris(mercaptoimidazolyl)borate compound  $[\text{In}(\text{Tm}^{\text{Me}})_2]\text{I}$ , the first  $\text{Tm}^{\text{R}}$  derivative of indium, has recently been reported (Dodds *et al.*, 2006).



The structure of the title compound was determined by single-crystal X-ray diffraction (Fig. 1), with selected bond

Received 24 February 2006  
Accepted 2 March 2006  
Online 8 March 2006



**Figure 1**  
A view of the title compound, (I), showing 50% probability displacement ellipsoids. [Symmetry code: (i)  $x, -y + \frac{3}{2}, z$ .]

lengths and angles shown in Table 1. The In atom in  $\text{In}(\text{Bm}^{\text{Me}})\text{Br}_2$  is coordinated by the two thione groups of a bis(mercaptoimidazolyl)borate ligand and two bromo ligands in a slightly distorted tetrahedral environment, with the angles subtended at the metal center in the range  $105\text{--}116^\circ$ . The two In–Br bond distances (Table 1) are only slightly shorter than the mean value found in the Cambridge Structural Database (CSD; Version 5.27, *ConQuest* Version 1.8; Allen, 2002) for such terminal interactions in four-coordinate indium complexes ( $2.516 \text{ \AA}$ ). The presence of a crystallographically imposed mirror plane, which contains the In, Br and B atoms and which bisects the molecule, results in the observation of a unique In–S bond length of  $2.4407 (11) \text{ \AA}$ . This value is significantly shorter than those in either  $[\text{In}(\text{Tm}^{\text{Me}})_2]\text{I}$  [ $2.603 (8)\text{--}2.623 (8) \text{ \AA}$ ; Dodds *et al.*, 2006] or the only four complexes of indium containing simple thioureas or heterocyclic thiones that are present in the CSD, all of which are, not surprisingly, five- or six-coordinate species:  $\text{In}\{\text{SC}(\text{NMe}_2)_2\}_2\text{Cl}_3$  [ $2.521 (2)$  and  $2.531 (2) \text{ \AA}$ ; Beddoes *et al.*, 1991],  $\text{In}\{\text{SC}(\text{NH}_2)_2\}_3\text{Cl}_3$  [ $2.574 (2)\text{--}2.613 (2) \text{ \AA}$ ; Malyarik *et al.*, 1992] and  $\text{In}(\text{dmit})_2\text{X}_3$  ( $\text{X} = \text{Cl}$  and  $\text{Br}$ ;  $2.516 (1)\text{--}2.529 (2) \text{ \AA}$ ; Williams *et al.*, 1999).

## Experimental

Toluene (5 ml) was added to a mixture of  $\text{InBr}_3$  (0.125 g, 0.353 mmol) and  $\text{Na}(\text{Bm}^{\text{Me}})$  (0.074 g, 0.282 mmol), resulting in the immediate formation of a white solid suspended in a colorless solution. The suspension was stirred for an additional 4 h, after which the product was isolated by filtration, washed with water (5 ml) and dried *in vacuo* for 22 h (0.123 g, 85%). M.p.  $482\text{--}485 \text{ K}$  (decomposition).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.71 (s, 12H,  $\text{CH}_3$ ), 6.90 (*d*,  $^3J_{\text{H-H}} = 2.0 \text{ Hz}$ , 4H, imidazole H), 7.06 (*d*,  $^3J_{\text{H-H}} = 2.0 \text{ Hz}$ , 4H, imidazole H), BH not observed.  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  36.2 (*q*,  $^1J_{\text{C-H}} = 143 \text{ Hz}$ , 4C,  $\text{CH}_3$ ), 122.2 (*d*,  $^1J_{\text{C-H}} = 205 \text{ Hz}$ , 4C, imidazole C), 126.0 (*d*,  $^1J_{\text{C-H}} = 193$ , 4 C, imidazole C), C=S not observed. IR ( $\text{cm}^{-1}$ ): 3157 (*m*), 3134 (*m*), 2925 (*w*), 2483 (*m*), 2419 (*m*), 2365 (*m*), 2342 (*w*), 1554 (*m*), 1468 (*s*), 1400 (*w*), 1379

(*w*), 1342 (*w*), 1302 (*w*), 1192 (*w*), 1172 (*m*), 1120 (*s*), 1016 (*w*), 718 (*s*), 467 (*w*). Analysis calculated for  $\text{C}_8\text{H}_{12}\text{BBr}_2\text{InN}_4\text{S}_2$ : C 18.7, H 2.4, N 11.0; found: C 18.9, H 2.3, N 10.5%.

## Crystal data

$[\text{InBr}_2(\text{C}_8\text{H}_{12}\text{BN}_4\text{S}_2)]$   
 $M_r = 513.79$   
Orthorhombic, *Pnma*  
 $a = 8.6314 (11) \text{ \AA}$   
 $b = 13.3019 (18) \text{ \AA}$   
 $c = 13.891 (3) \text{ \AA}$   
 $V = 1594.9 (5) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 2.14 \text{ Mg m}^{-3}$

Cu  $K\alpha$  radiation  
Cell parameters from 25 reflections  
 $\theta = 4.6\text{--}19.9^\circ$   
 $\mu = 20.06 \text{ mm}^{-1}$   
 $T = 296 (2) \text{ K}$   
Irregular fragment, colorless  
 $0.41 \times 0.16 \times 0.06 \text{ mm}$

## Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
Absorption correction: analytical (Katayama, 1986)  
 $T_{\text{min}} = 0.054$ ,  $T_{\text{max}} = 0.304$   
1579 measured reflections  
1579 independent reflections

1351 reflections with  $I > 2\sigma(I)$   
 $\theta_{\text{max}} = 69.9^\circ$   
 $h = 0 \rightarrow 10$   
 $k = 0 \rightarrow 16$   
 $l = 0 \rightarrow 16$   
3 standard reflections  
frequency: 60 min  
intensity decay: 1.7%

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.030$   
 $wR(F^2) = 0.083$   
 $S = 1.03$   
1579 reflections  
90 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 1.1144P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.54 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.88 \text{ e \AA}^{-3}$   
Extinction correction: *SHELXL97*  
Extinction coefficient: 0.00118 (9)

**Table 1**  
Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

In–S	2.4407 (11)	In–Br1	2.5018 (8)
In–Br2	2.4864 (9)		
$\text{S}^i\text{--In--S}$	115.78 (6)	$\text{S--In--Br1}$	105.23 (3)
$\text{S--In--Br2}$	109.45 (3)	$\text{Br2--In--Br1}$	111.60 (3)

Symmetry code: (i)  $x, -y + \frac{3}{2}, z$ .

The H atoms were constrained using a riding model. The ring C–H bond lengths were fixed at  $0.93 \text{ \AA}$ , with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ , and the B–H bond lengths were fixed at  $0.97 \text{ \AA}$ , with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{B})$ . The methyl C–H bond lengths were fixed at  $0.96 \text{ \AA}$ , with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ . For the methyl group, an idealized tetrahedral geometry was used, and the torsion angle about the C–N bond was refined.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The title compound was synthesized and the crystals were prepared by Sarah Hill of the Chemistry Department of The University of North Carolina at Charlotte. The authors thank the Camille and Henry Dreyfus Foundation Inc. for a Henry Dreyfus Teacher–Scholar Award to DR, Research Corpora-

tion for a Cottrell College Science Award, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (award No. CHE-0316723) for support of this research. This work was also supported, in part, by funds provided by The University of North Carolina at Charlotte.

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