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# The Preparation and Structure of Tris[bis(pyrazolyl)borate]indium(III)

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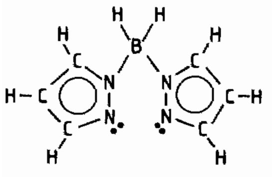
## Abstract

The compound $In[(pz)_2BH_2]_3$ (pz = 1-pyrazolyl, $C_3H_3N_2^-$) was prepared from $In(NO_3)_3$ and $K[(pz)_2BH_2]$ in water, and characterised by spectroscopic and X-ray methods. Crystals are orthorhombic, $Pna2_1$, $a = 20.279(4)$, $b = 8.884(2)$, $c = 13.411(2)$ Å; $R = 0.0285$. Individual molecules contain a near-regular six-coordinate indium atom with In–N (av.) 2.241(5) Å. The pyrazolyl borate ligands are puckered, with dihedral angles between the two rings of each ligand in the range 133–144°.

## Introduction

Neutral tris-chelate β-ketoenolate complexes of metal ions, such as $M(acac)_3$, have been extensively studied for many years since they are usually stable, easily-prepared materials with interesting properties. It is therefore surprising that related neutral complexes containing the Trofimenko ligand $[(pz)_2BH_2]^-$ (**1**) are essentially unknown, since acac⁻ and **1** are formally analogous in that they are both uninegative bidentate ligands which give six-membered chelate rings [1]. The major difference between them is that unlike the planar acac⁻ the ligand **1** is usually puckered to provide a suitable 'bite' while maintaining tetrahedral angles at the boron atom. This makes **1** a bulkier ligand than acac⁻ and so leads to more crowded coordination spheres. As a consequence most of the transition element complexes incorporating ligand **1** are four-coordinate square-planar or tetrahedral M(II) species [1, 2]. However the synthesis of some anionic, tris-chelate complexes $[M\{(pz)_2BH_2\}_3]^-$ has been reported [3], and an example with M = V structurally characterised [4], showing that three ligands **1** can be accommodated about a larger metal ion.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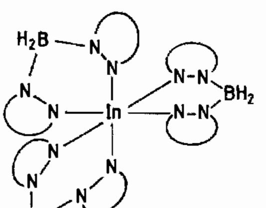
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As an extension of our previous work on pyrazolyl borate complexes of tin [5], we now report the preparation and full characterisation of $In[(pz)_2BH_2]_3$ (**2**) the first neutral tris-chelate complex of this type to be structurally characterised.

## Experimental

$K[(pz)_2BH_2]$ was prepared by the standard method [6]. Microanalysis was performed by the University of Otago Microanalytical service. The $^{115}In$ NMR spectra were obtained on a Jeol FX90Q spectrometer operating at a resonant frequency of 19.59 MHz and mass spectra on a Varian CH5 spectrometer.

### *Preparation of In[(pz₂)BH₂]₃ (2)*

A solution of $In(NO_3)_3$ (0.41 g, 1.37 mmol) in water (5 ml) was added to a solution of $K[(pz)_2BH_2]$ (0.74 g, 4.01 mmol) in water (10 ml). After 5 min the white precipitate was filtered off, dried and recrystallised from $CH_2Cl_2$/petroleum spirit to give white crystals of **2**. Yield: 55%. *Anal.* Found: C, 38.47; H, 4.78; N, 28.66%; $M = 555$ (P+, mass spectrum). Calc. for $C_{18}H_{24}B_3N_{12}In$: C, 38.90; H, 4.35; N, 30.25%; $M = 555$. IR (KBr disc): $\nu(BH_2)$ 2300(s), 2150(w) cm⁻¹. NMR ($CDCl_3$ solution): $^1H$, δ 7.71, 7.02, (both d, $J$ 2.05 Hz, 3-H, 5-H), 6.16 (t, $J$ 2.05 Hz, 4-H); $^{13}C$ δ 141.05, 137.99 (3-C, 5-C), 104.89 (4-C); $^{115}In$: δ 120 (*versus* aqueous $In(NO_3)_3$), $\nu_{1/2}$ 4300 Hz.

### *X-ray Structure of 2*

A wedge-shaped crystal 0.65 × 0.50 × 0.40 mm was obtained from $CH_2Cl_2$/hexane. Preliminary precession photography indicated orthorhombic symmetry. Lattice parameters were determined using 25 high-angle reflections, accurately centred on a Nicolet P3 diffractometer with monochromated X-radiation (λ = 0.7107 Å).

*Crystal data*: $C_{18}H_{24}B_3N_{12}In$, $M_r$ 555.72, orthorhombic, $Pna2_1$, $a = 20.279(4)$, $b = 8.884(2)$, $c =$

0020-1693/88/$3.50

TABLE I. Final Positional Parameters for $In[(pz)_2BH_2]_3$

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| In(1) | 0.15204(1) | 0.08813(3) | 0.25000 | C(33) | 0.2755(3) | 0.2838(7) | 0.3379(5) |
| B(1) | 0.0169(3) | −0.0219(8) | 0.3968(5) | N(41) | 0.1986(2) | −0.1301(5) | 0.1985(4) |
| N(11) | 0.0573(2) | −0.0277(5) | 0.2168(3) | N(42) | 0.2650(2) | −0.1534(6) | 0.1859(4) |
| N(12) | 0.0135(2) | −0.0755(5) | 0.2868(3) | C(41) | 0.2765(3) | −0.3032(7) | 0.1815(5) |
| C(11) | −0.0333(2) | −0.1594(6) | 0.2421(6) | C(42) | 0.2184(3) | −0.3805(8) | 0.1934(6) |
| C(12) | −0.0200(3) | −0.1706(7) | 0.1420(5) | C(43) | 0.1715(3) | −0.2675(8) | 0.2040(5) |
| C(13) | 0.0375(3) | −0.0849(7) | 0.1299(5) | B(3) | 0.0425(4) | 0.3634(8) | 0.1658(5) |
| N(21) | 0.1437(2) | −0.0079(5) | 0.4022(4) | N(51) | 0.1412(2) | 0.2057(5) | 0.1034(4) |
| N(22) | 0.0858(2) | −0.0610(5) | 0.4417(4) | N(52) | 0.0987(2) | 0.3240(6) | 0.0906(4) |
| C(21) | 0.0988(3) | −0.1310(7) | 0.5276(5) | C(51) | 0.1056(3) | 0.3817(7) | −0.0014(5) |
| C(22) | 0.1658(3) | −0.1253(7) | 0.5469(5) | C(52) | 0.1535(3) | 0.2984(7) | −0.0508(5) |
| C(23) | 0.1916(3) | −0.0479(6) | 0.4657(4) | C(53) | 0.1751(3) | 0.1911(7) | 0.0175(5) |
| B(2) | 0.3133(3) | −0.0228(8) | 0.1623(5) | N(61) | 0.1119(2) | 0.2983(5) | 0.3188(3) |
| N(32) | 0.3122(2) | 0.0986(5) | 0.2460(6) | N(62) | 0.0721(2) | 0.3989(5) | 0.2707(3) |
| N(31) | 0.2563(2) | 0.1710(5) | 0.2774(3) | C(61) | 0.0533(3) | 0.5078(8) | 0.3343(5) |
| C(31) | 0.3647(3) | 0.1669(7) | 0.2862(5) | C(62) | 0.0822(3) | 0.4817(8) | 0.4252(5) |
| C(32) | 0.3441(3) | 0.2860(8) | 0.3456(5) | C(63) | 0.1173(3) | 0.3492(8) | 0.4135(5) |

TABLE II. Selected Bond Lengths and Angles for $In[(pz)_2BH_2]_3$

| | | | |
|---|---|---|---|
| Bond lengths (Å) | | | |
| In–N(11) | 2.224(5) | B(1)–N(12) | 1.551(8) |
| In–N(21) | 2.218(5) | B(1)–N(22) | 1.562(8) |
| In–N(31) | 2.269(4) | B(2)–N(32) | 1.556(9) |
| In–N(41) | 2.264(5) | B(2)–N(42) | 1.551(8) |
| In–N(51) | 2.237(5) | B(3)–N(52) | 1.561(8) |
| In–N(61) | 2.236(5) | B(3)–N(62) | 1.562(8) |
| N(1)–N(2)[a] | 1.369(6) | N(1)–C(3)[a] | 1.343(8) |
| N(2)–C(1)[a] | 1.344(9) | C(1)–C(2)[a] | 1.379(9) |
| C(2)–C(3)[a] | 1.392(8) | | |
| Bond angles (°) | | | |
| N(11)–In(1)–N(21) | 86.6(2) | N(12)–B(1)–N(22) | 109.8(5) |
| N(11)–In(1)–N(31) | 170.9(2) | N(32)–B(2)–N(42) | 111.3(5) |
| N(11)–In(1)–N(41) | 84.4(2) | N(52)–B(3)–N(62) | 110.2(5) |
| N(11)–In(1)–N(51) | 87.5(2) | N(11)–In(1)–N(61) | 98.9(2) |
| N(21)–In(1)–N(31) | 92.7(2) | N(21)–In(1)–N(41) | 89.0(2) |
| N(21)–In(1)–N(51) | 168.7(2) | N(21)–In(1)–N(61) | 85.1(2) |
| N(31)–In(1)–N(41) | 86.5(2) | N(31)–In(1)–N(51) | 94.7(2) |
| N(31)–In(1)–N(61) | 90.1(2) | N(41)–In(1)–N(51) | 99.9(2) |
| N(41)–In(1)–N(61) | 173.0(2) | N(51)–In(1)–N(61) | 86.4(2) |

[a] Averaged over all rings.

13.411(2) Å, $U = 2416.1(9)$ Å$^3$. $D_c = 1.528$, $D_m = 1.50$ g cm$^{-3}$, $Z = 4$. $F(000)$ 1120, $\mu(\text{Mo K}\alpha) = 9.8$ cm$^{-1}$, $T = 163$ K.

A total of 2452 unique reflections were collected in the range $5° < 2\theta < 52°$ and were corrected for Lorentz, polarisation and absorption effects (based on a series of $\phi$ scans). Of these, 2101 had $I > 3\sigma(I)$, and were used in all calculations.

The position of the In atom was located from a Patterson map. A subsequent difference map was complicated by false symmetry, but the complete molecule was gradually developed. In the final cycles of full-matrix least-squares refinement the In atom was assigned an anisotropic temperature factor, while other atoms were isotropic, with H atoms included in calculated positions with common temperature factors for each type. The refinement converged at $R = 0.0285$, $R_w = 0.0281$ where $w = [\sigma^2(F) + 0.00016\ F^2]^{-1}$, largest $\Delta/\sigma$ 0.01, largest feature in final difference map 0.7 e Å$^{-3}$. A refinement cycle with inverted coordinates gave higher $R$ values showing the original polarity of the crystal was the correct one. All calculations were performed with SHELX-76 [7], using scattering factors and $\Delta f'$ and $\Delta f''$ values

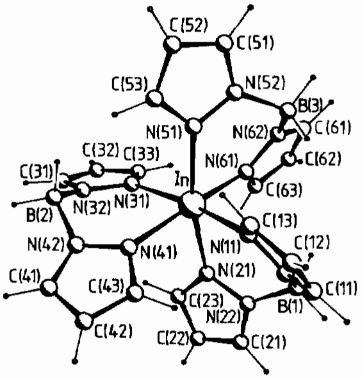

Fig. 1. A view of In$[(pz)_2BH_2]_3$, showing atom labelling.

taken from International Tables, while equations of planes were calculated using PARST [8]. Final positional parameters are given in Table I, with selected bond parameters in Table II. The geometry and atom numbering is shown in Fig. 1 while Fig. 2 is a stereo diagram viewed down a pseudo three-fold axis of the molecule.

## Results and Discussion

The preparation of In$[(pz)_2BH_2]_3$ (2) was straightforward, the product precipitating from an aqueous solution containing the ligand $[(pz)_2BH_2]^-$ and $In^{3+}$ ions in the stoichiometric ratio. The crude product is fairly soluble in polar organic solvents and could be recrystallised from $CH_2Cl_2$/hexane to give high-melting white crystals. The preparation in aqueous solution reflects good stability to hydrolysis, in contrast to anionic tris-chelate analogues such as K[Ni$\{(pz)_2BH_2\}_3$] which react instantly with water [3a] although the corresponding $Et_4N^+$ salts are apparently more stable [3b].

The spectroscopic properties of 2 are given in 'Experimental'. A clean mass spectrum was obtained showing a parent ion and fragment ions resulting from successive losses of $(pz)BH_2$ and $(pz)_2BH_2$. The $^1$H and $^{13}$C NMR spectra were similar to those in which $[(pz)_2BH_2]^-$ is attached to tin [5]. The assignment of the H and C signals from the 4-position of the ring is obvious but those from the 3,5-positions are not readily distinguished [2, 9].

The $^{115}$In NMR spectrum gave a broad signal at 120 ± 10 ppm downfield from aqueous $In^{3+}$. There appear to be few reported NMR spectra for six-coordinate indium, most attention having been devoted to $InX_4^-$ species [10]. Little can therefore be said about the $\delta$ value observed for 2, but the broadness of the signal (4300 Hz compared with 2000 Hz for $In(H_2O)_6{}^{3+}$) indicates that the coordination environment is markedly distorted from regular octahedral, a conclusion consistent with the structural results in the solid state.

The structure of In$[(pz)_2BH_2]_3$ shows the metal atom to be six-coordinated by the six nitrogen atoms of three $[(pz)_2BH_2]^-$ ligands. In–N bonds range from 2.219(5) to 2.268(5) Å (average 2.241(5) Å) and N–In–N angles lie between 84.5(2)° and 99.9(2)° for adjacent sites and 168.7(2)° to 173.0(2)° for opposite sites, so distortions from octahedral geometry are significant. The In–O distances in $In(acac)_3$ are 2.128 Å [11] so the In–N distances in 2 are probably about 0.1 Å longer than would be expected in a less sterically crowded system. All the pyrazolyl rings are essentially planar but the In and B atoms are twisted from these planes by 0.10–0.53 and 0.10–0.27 Å respectively. The dihedral angles between pyrazolyl planes within each ligand are 133.8° (rings 1, 2) 141.2° (rings 3, 4) and 143.9° (rings 5, 6). These values are much larger than are usually found for $[(pz)_2BH_2]^-$ ligands in less crowded molecules; for example in $Me_2ClSn[(pz)_2BH_2]$, with a metal atom of comparable size, the dihedral angle between the pz rings is 119° [5], and it is even lower in $Cr[(pz)_2BH_2]_2$ at 115° [4]. In 2, the puckering is not in the same sense for each of the ligands. From Fig. 2 it can be seen that B(2) and B(3) are displaced from their ligands in a clockwise

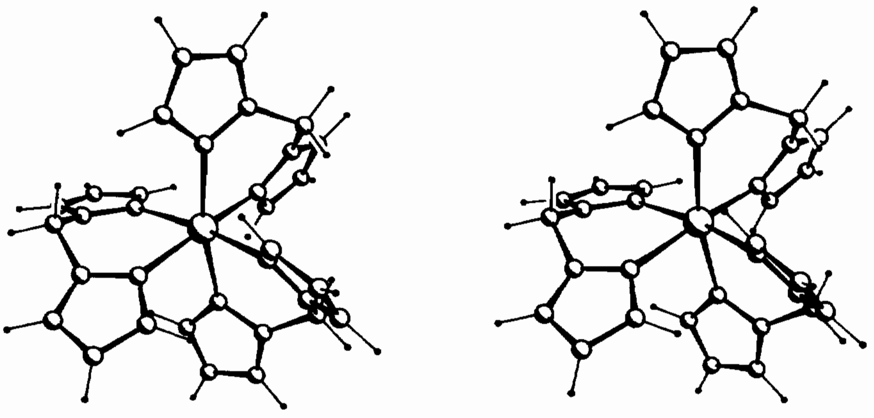

Fig. 2. A stereo view of 2 viewed down the pseudo three-fold axis.

sense, while B(1) is displaced in the opposite direction.

A comparison of the structure of 2 with that of $[V\{(pz)_2BH_2\}_3]^-$ shows close similarities [4]. The V–N distances are slightly shorter (2.17 Å) than the equivalent In–N (2.24 Å) reflecting the smaller radius of V(II), *cf.* In(III). The puckering of the individual ligands is more variable in the vanadium example, with dihedral angles between the two halves of the ligands ranging from 128° to 158°, although again the bending is in the opposite sense for one of the ligands compared with the other two. This is therefore probably a necessary intramolecular consequence rather than a crystal packing effect.

The relatively long In–N bonds and the flattened ligands found in the structure of 2 can be understood in terms of a crowded coordination sphere. There has to be a compromise between a need to pucker the ligands to provide a good chelating geometry, while minimising inter-ligand interactions which would be best achieved by planar ligands. Only larger metal ions will therefore be able to form complexes of the type $M[(pz)_2BH_2]_3$ and consistent with this we find that $Ga^{3+}$ forms an analogue of 2, but the corresponding reaction of $Al^{3+}$ with $[(pz)_2BH_2]^-$ gives different, as yet uncharacterised, products.

## Supplementary Material

Full tables of crystallographic data are available on request from the authors.

## Acknowledgements

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