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Synthesis and Solid-State Structure of $[HB(3,5\text{-}Me_2pz)_3]In(S_4)(3,5\text{-}Me_2pzH)$ (pz = Pyrazolyl): The First Neutral Indium Polysulfide Complex

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Introduction

Reports of group 13 metal polychalogenide complexes have recently been increasing.[1] One of the reasons for the interest in this area stems from the potential of group 13 metal polychalogenide complexes to serve as precursors for the production of thin-films,[2] but to date, all of the complexes have been ionic. We hoped to exploit the demonstrated ability of poly(pyrazolyl) borate ligands to stabilize main group metal complexes[3] to synthesize *neutral* group 13 metal polychalogenide complexes. We report here the synthesis and characterization of $[HB(3,5\text{-}Me_2pz)_3]In(S_4)(3,5\text{-}Me_2pzH)$.

Experimental Section

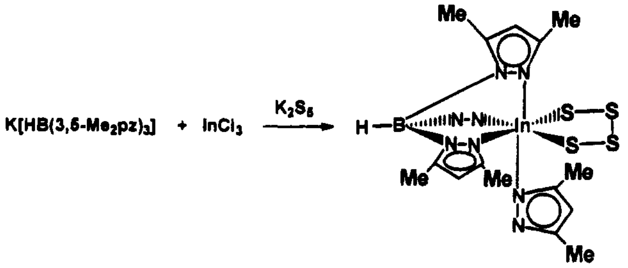
General. All solvents were dried over the appropriate desiccants and degassed prior to use. The following materials were obtained from Aldrich: $3,5\text{-}Me_2\text{-}pzH$, KBH_4, and $K[HB(^sBu)_3]$ (1 M in THF). Sulfur was obtained from Baker. All of these materials were used as received. Anhydrous $InCl_3$ was obtained from both Strem and Cerac. $K[HB(3,5\text{-}Me_2pz)_3]$[4] was synthesized by literature methods. K_2S_n was synthesized via the previously reported methods except that $K[HB(^sBu)_3]$ was substituted for superhydride.[5]

$[HB(3,5\text{-}Me_2pz)_3]In(S_4)(3,5\text{-}Me_2pzH)$. A Schlenk flask was charged with $InCl_3$ (0.22 g, 1.0 mmol). The solid was dissolved in THF (30 mL), and $K[HB(3,5\text{-}Me_2pz)_3]$ (0.34 g, 1.0 mmol) was added slowly to the stirred solution via a solid addition tube. The stirring was continued while a THF (10 mL) suspension of K_2S_5 (1.0 mmol) was prepared. The orange slurry of K_2S_5 was then added to the stirred solution of $[HB(3,5\text{-}Me_2pz)_3]InCl_2(THF)$ to yield a yellow solid and solution. The mixture was then heated at reflux overnight. A large amount of yellow solid precipitated. The solvent was removed under vacuum and the resulting yellow solid extracted with CH_2Cl_2 (40 mL). The remaining solid was filtered away and the solvent removed under vacuum to yield a yellow solid (0.13 g, 20%). Both the analytical sample and the X-ray quality crystals were obtained by recrystallization of the crude product from CH_2Cl_2/hexanes. ^1H NMR ($CDCl_3$, 23 °C): δ 11.45 (s, NH, 1H), 5.74 (s, 4-pz-H, 3H), 5.70 (s, 4-pz-H, 1H), 2.38 (br, pz-Me, 9H), 2.36 (s, pz-Me, 3H), 2.27 (br s, pz-Me, 3H), 2.10 (br s, pz-Me, 6H), 0.95 (br s, pz-Me, 3H). ^1H NMR ($CDCl_3$, −53 °C): δ 11.44 (s, NH, 1H), 5.77 (s, 4-pz-H, 1H), 5.74 (s, 4-pz-H, 2H), 5.70 (s, 4-pz-H, 1H), 2.41 (s, pz-Me, 3H), 2.38 (s, pz-Me, 6H), 2.34 (s, pz-Me, 3H), 2.26 (s, pz-Me, 3H), 1.95 (s, pz-Me, 6H), 0.86 (s, pz-Me, 3H). Mass spectrum (*m/z*): 540, $[HB(3,5\text{-}Me_2pz)_3]In(S_4)$; 476, $[HB(3,5\text{-}Me_2pz)_3]In(S_2)$. Anal. Calcd for $C_{20}H_{30}BInN_8S_4$: C, 37.75; H, 4.75; N, 17.61. Found: C, 38.08; H, 4.58; N, 17.54.

Crystallography of $[HB(3,5\text{-}Me_2pz)_3]In(S_4)(3,5\text{-}Me_2pzH)$. A yellow irregular crystal of $[HB(3,5\text{-}Me_2pz)_3]In(S_4)(3,5\text{-}Me_2pzH)$ having approximate dimensions of $0.20 \times 0.20 \times 0.30$ mm^3 was mounted in a glass capillary with its long axis roughly parallel to the φ axis of the goniometer. The unit cell dimensions were determined and refined from 25 general reflections. From the systematic absences and from subsequent least-squares refinement, the space group of the monoclinic cell was determined to be $P2_1/c$ (No. 14). Table 1 shows parameters of the crystal, data collection, and refinement, and Table 2 shows positional parameters. The data were collected over the range $4 < 2\theta \leq 50$ ($\pm h$, $+k$, $+l$). A total of 9064 reflections were collected, of which 4721 were unique and not systematically absent. Only the 3973 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. As a check on crystal and electronic stability, three representative reflections were measured every 120 min. The intensities of these standards remained constant within experimental error throughout data collection. Lorentz and polarization corrections were applied to the data. A semiempirical absorption correction was made. The structure was solved using the Patterson heavy-atom method, which revealed the position of the indium atom. The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. Only a few hydrogen atoms were located from the difference Fourier maps phased on the non-hydrogen atoms, and the rest were placed in calculated positions (d(C−H) = 0.95 Å). The hydrogen atoms were included in the last cycles of the refinement but restrained to ride on the atom to which they are bonded. Anomalous dispersion effects were included in F_c.[6] All calculations were performed on a VAX computer using MolEN.[7]

Results and Discussion

The reaction of $[HB(3,5\text{-}Me_2pz)_3]InCl_2$ (prepared in situ) with K_2S_5 yields $[HB(3,5\text{-}Me_2pz)_3]In(S_4)(3,5\text{-}Me_2pzH)$. The coordinated $3,5\text{-}Me_2pzH$ group is apparently derived from decomposition of the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand. Employing $[HB(3,5\text{-}Me_2pz)_3]InCl_2(3,5\text{-}Me_2pzH)$ as the indium starting material resulted in increased yield of the product from 20% to 47%. The formation of $[HB(3,5\text{-}Me_2pz)_3]In(S_4)(3,5\text{-}Me_2pzH)$, even in the absence of $3,5\text{-}Me_2pzH$, demonstrates again the propensity of tris(pyrazolyl)borate complexes of indium to be six-coordinate. We have shown previously that the reaction of $K[HB(3,5\text{-}Me_2pz)_3]$ and $InCl_3$ in toluene yields $[HB(3,5\text{-}Me_2pz)_3]InCl_2(3,5\text{-}Me_2pzH)$,[3b] and other isolated complexes of this type, such as $[HB(3,5\text{-}Me_2pz)_3]InCl_2(NCCH_3)$[3d] and $[HB(3,5\text{-}Me_2pz)_3]In[S_2C_2(CN)_2](THF)$,[3c] are also Lewis base adducts.



Crystalline $[HB(3,5\text{-}Me_2pz)_3]In(S_4)(3,5\text{-}Me_2pzH)$ is air stable, but solutions of this complex degrade slowly. Attempts to sublime $[HB(3,5\text{-}Me_2pz)_3]In(S_4)(3,5\text{-}Me_2pzH)$ resulted only in decomposition. Thermal gravimetric analysis of [HB(3,5-Me₂-

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Table 1. Crystallographic Data for [HB(3,5-$Me_2pz)_3$]In(S_4)(3,5-Me_2pzH)

formula	$C_{20}H_{30}BInN_8S_4$	V, Å^3	2786.3
fw	636.40	Z	4
crystal system	monoclinic	D(calc), g cm^{-3}	1.52
space group	$P2_1/c$	λ(Mo Kα), Å	0.710 73
a, Å	12.732(5)	temp, K	296
b, Å	11.214(4)	R_F[a]	0.048
c, Å	19.583(3)	R_{wF}[b]	0.061
β, deg	94.80(1)		

[a] $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_{wF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F)$.

Table 2. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B (Å^2)
In1	0.23981(2)	0.19188(3)	0.38289(1)	2.492(6)
S2	0.1832(1)	0.2115(1)	0.50425(6)	4.19(3)
S3	0.1079(2)	0.3698(2)	0.5025(1)	6.91(4)
S4	0.2122(2)	0.4831(2)	0.4626(1)	7.61(6)
S5	0.2304(1)	0.4176(1)	0.36453(8)	4.95(3)
N6	0.0655(3)	0.1681(4)	0.3366(2)	3.28(8)
N7	−0.0055(3)	0.2415(4)	0.3636(2)	3.37(8)
N13	0.4156(3)	0.1701(4)	0.4118(2)	3.03(8)
N14	0.4660(3)	0.0781(4)	0.3814(2)	3.33(8)
N20	0.2439(3)	−0.0122(4)	0.3896(2)	3.16(8)
N21	0.3203(3)	−0.0708(4)	0.3571(2)	3.11(8)
N27	0.2882(3)	0.1601(4)	0.2753(2)	3.00(8)
N28	0.3624(3)	0.0729(4)	0.2657(2)	2.90(7)
C8	−0.1056(4)	0.2226(5)	0.3352(3)	4.3(1)
C9	−0.0969(4)	0.1314(6)	0.2884(3)	4.5(1)
C10	0.0076(4)	0.1015(5)	0.2902(3)	3.7(1)
C11	0.0559(5)	0.0072(6)	0.2496(3)	5.4(1)
C12	−0.1945(5)	0.2929(7)	0.3572(5)	6.6(2)
C15	0.5665(4)	0.0741(5)	0.4082(3)	4.4(1)
C16	0.5816(5)	0.1649(6)	0.4569(3)	4.8(1)
C17	0.4860(4)	0.2217(5)	0.4576(3)	3.7(1)
C18	0.4580(5)	0.3281(7)	0.4982(3)	6.0(2)
C19	0.6452(5)	−0.0130(7)	0.3860(5)	7.0(2)
C22	0.2999(4)	−0.1879(5)	0.3560(3)	3.8(1)
C23	0.2112(5)	−0.2064(4)	0.3876(3)	4.1(1)
C24	0.1774(4)	−0.0963(5)	0.4086(3)	4.0(1)
C25	0.0815(4)	−0.0668(6)	0.4452(3)	5.5(1)
C26	0.3692(5)	−0.2766(5)	0.3237(4)	4.9(1)
C29	0.3719(4)	0.0618(5)	0.1975(2)	3.7(1)
C30	0.3073(4)	0.1421(6)	0.1636(2)	4.4(1)
C31	0.2563(4)	0.2028(5)	0.2130(3)	3.7(1)
C32	0.1730(5)	0.2977(6)	0.2017(3)	5.2(1)
C33	0.4454(5)	−0.0278(5)	0.1699(3)	5.0(1)
B34	0.4096(4)	−0.0026(5)	0.3269(3)	3.2(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

pz)$_3$]In(S_4)(3,5-Me_2pzH) showed two weight loss episodes that do not correspond to the loss of any reasonable fragment of the complex.

The room temperature ^{1}H NMR spectrum of [HB(3,5-$Me_2pz)_3$]In(S_4)(3,5-Me_2pzH) contains several board resonances that make difficult the definite assignment of the structure of the complex in solution. Cooling of the sample causes the broad resonances to resolve into sharp resonances that are consistent with the solid-state structure (vide infra). The dynamic process responsible for the line broadening at ambient temperature is presumably reversible dissociation of the 3,5-Me_2pzH ligand.

Structure of [HB(3,5-$Me_2pz)_3$]In(S_4)(3,5-Me_2pzH). X-ray quality crystals of [HB(3,5-$Me_2pz)_3$]In(S_4)(3,5-Me_2pzH) were obtained from carefully layering hexanes on to a concentrated solution of the crude product in CH_2Cl_2. An ORTEP diagram of the molecule is shown in Figure 1, and selected bond distances and angles are shown in Table 3. The structure has a distorted octahedral geometry about indium consisting of four nitrogen and two sulfur donor atoms. The three In−N bond distances from the [HB(3,5-$Me_2pz)_3$]$^-$ ligand average 2.28 Å while the fourth, from a 3,5-Me_2pzH ligand, is longer at 2.342(4) Å. These distances are similar to those found in [HB(3,5-$Me_2pz)_3$]$InCl_2$(NCMe).[3d]

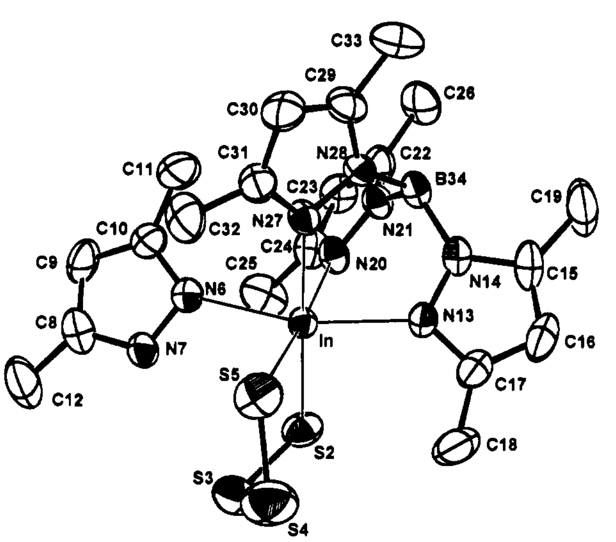

Figure 1. ORTEP drawing of [HB(3,5-$Me_2pz)_3$]In(S_4)(3,5-Me_2pzH).

Table 3. Selected Bond Distances (Å) and Bond Angles (deg)

	Distances		
In1−S2	2.550(1)	In1−N27	2.271(4)
In1−S5	2.558(2)	S2−S3	2.017(3)
In1−N6	2.342(4)	S3−S4	2.041(3)
In1−N13	2.276(4)	S4−S5	2.088(3)
In1−N20	2.293(4)		
	Angles		
S2−In1−S5	91.85(5)	N6−In1−N13	164.8(1)
S2−In1−N6	92.2(1)	N6−In1−N20	85.7(1)
S2−In1−N13	97.3(1)	N6−In1−N27	86.8(1)
S2−In1−N20	92.3(1)	N13−In1−N20	82.0(1)
S2−In1−N27	175.9(1)	N13−In1−N27	82.9(1)
S5−In1−N6	91.5(1)	N20−In1−N27	83.7(1)
S5−In1−N13	100.1(1)	S2−S3−S4	103.4(1)
S5−In1−N20	175.1(1)	S3−S4−S5	105.0(1)
S5−In1−N27	92.2(1)		

The InS_4 ring is arranged in a half-chair configuration with the S3 and S4 atoms 0.755(2) and 0.3734(2) Å above and below the S2InS5 plane. The S−In−S angle of 91.85(5)° and In−S bond lengths are similar to those observed in InS_4 rings in other related indium polysulfide anions.[1b,c,f]

An interesting structural feature is that the orientation of the 3,5-Me_2pzH ligand is such that the 3-methyl group is placed between two of the rings on the [HB(3,5-$Me_2pz)_3$]$^-$ ligand. The proximity of this 3-methyl group to the ring currents of the two pyrazolyl rings causes its ^{1}H NMR resonance to be shielded (0.85 δ) when compared to similar methyl groups in normal environments. A similar shielding has been observed previously with [HB(3,5-$Me_2pz)_3$]In[$H_2B(pz)_2$]Cl.[3c]

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Supporting Information Available: Tables of complete data collection information, bond distances, angles, anisotropic thermal parameters, and positional parameters of H atoms (8 pages). Ordering information is given on any current masthead page.

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